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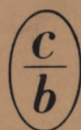
July, 1989

LITHOLOGY AND MINERAL RESOURCES

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A translation of *Litologiya i Poleznye Iskopaemye*

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ARID ZONES IN THE OCEAN. THEIR BOUNDARIES AND THE CONTRIBUTION OF EOLIAN MATERIAL TO OCEANIC SEDIMENTATION

B. P. Vasil'ev and O. A. Pomortsev

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In the article, we base the boundaries of arid zones in the ocean on the criterion used for their delin-
eation on the continents, the ratio of atmospheric sediments precipitated yearly to the total yearly amount
of evapotranspiration. It is shown that, in contrast to the continents, there are no characteristic oceanic
landforms and no special types of sediment formation peculiar to these zones only. On the basis of the
average yearly concentrations of atmospheric mineral aerosol and naturalistic observations on the
rewinning of sands, we calculated the total quantity of eolian terrigenous material entering the oceans.

Three types of natural zonalities, climatic, vertical, and circumcontinental, lie at the base of the theory of oceanic
sediment formation developed by A. P. Lisitsyn [13, 14]. In the final analysis, the combination of these types of
zonalities is believed to determine the type of sediment, the features of its granulometry, and its material composition.
The climatic zonality is believed to play a definitive role in the formation of oceanic sediments; and in the ocean, just
as on the continental block, three zonal climatic types of lithogenesis exists: glacial, arid, and azonal-volcanic-
sedimentary.

From our point of view, such an approach to oceanic sedimentogenesis can be validly criticized on the basis of
the theory of climatic types of lithogenesis put forward by N. M. Strakhov [21-26], who showed that a single oceanic
type of lithogenesis (outside zones of vulcanism) exists within oceans. The patterns basic to this type of lithogenesis are
determined not by climate but by the hydrodynamic regimes of the oceanic water bodies. The principal objections of
N. M. Strakhov to taking the climatic types of lithogenesis natural to the Earth's continental block and applying them
to oceans are put forward in [21-23]. They mainly concern the fact that the climatic types of lithogenesis in the ocean
have been, to a large degree, artificially distinguished from one another. There has been a distortion of the principles
and criteria for identifying such types on continents; in the oceans, the types involved do not bear the characteristic
features of continental lithogenesis. This is what permits them to be assigned to one and the same climatic type. By
analyzing lithogenesis of the arid type, N. M. Strakhov persuasively demonstrated the groundlessness and artificiality
of such a distinction in the ocean; this is expressed in inconsistency found in the behavior of boundaries of arid-type
lithogenesis in the ocean precisely along the zero isoline for the evaporation-sediment difference, it is expressed in the
absence of the authigenic minerals (well dissolved salts and indicators of continental lithogenesis of the arid type) in the
arid zones of the ocean, and it is expressed in the unsoundness of explaining features of oceanic sedimentation, primarily
the unsoundness of explaining the distribution of types of deposits and the rates of sediment accumulation in arid zones
from the doctrinal positions associated with climatic types of lithogenesis [22]. Despite the exhaustive nature of the
analysis which has carried out, an analysis which brings one to the entirely valid conclusion that arid types of lithogenesis
do not exist in the ocean, some very important questions remain which require more careful consideration. The present
article, being a continuation of the ideas of N. M. Strakhov, compensates for certain problems associated with sediment
formation in the arid zones of the ocean.

Boundaries of Arid Zones in the Oceans

According to the theory of A. P. Lisitsyn [13, 14], the arid type of lithogenesis in the ocean coincides, just as
it does on the continent, with regions of ocean where evaporation through the year exceeds the sum of meteoric
sediments. On the map of types of lithogenesis in the ocean presented in A. P. Lisitsyn's reports [13, 14], this thesis is

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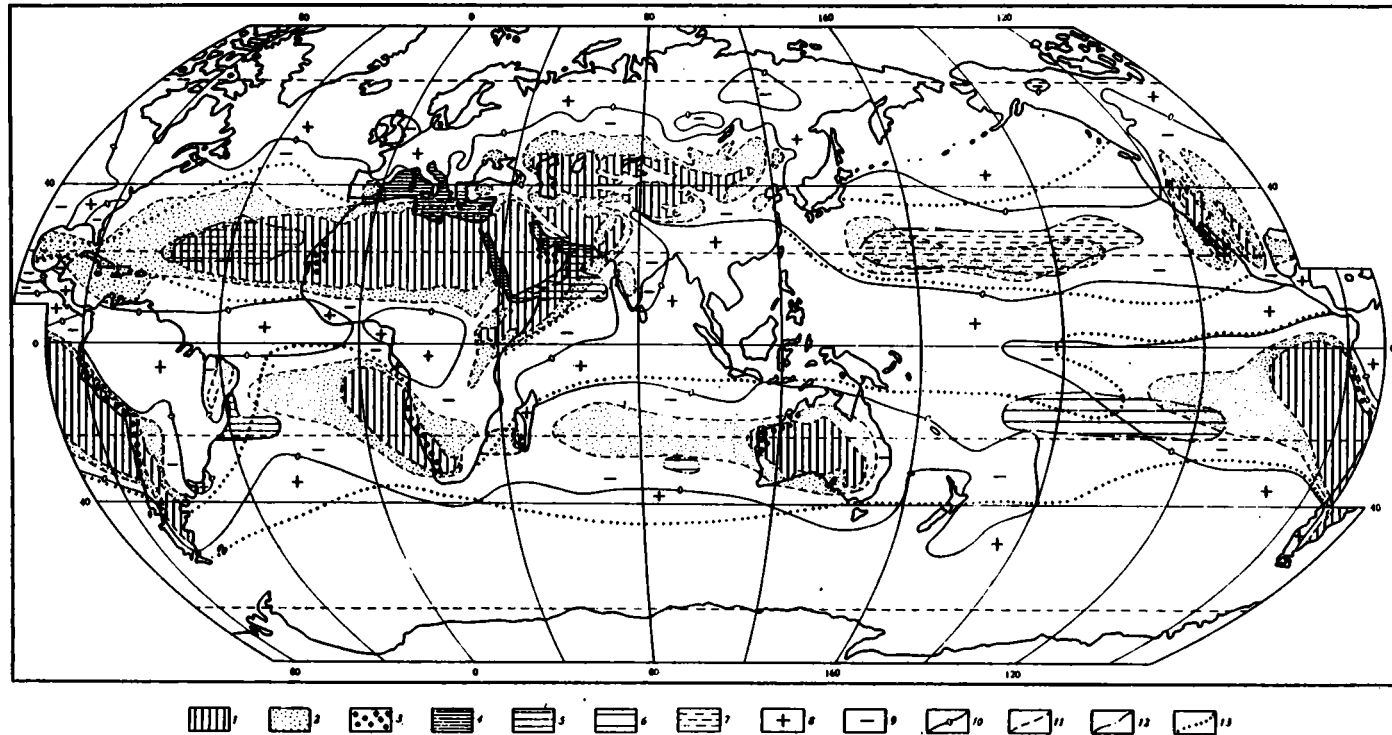


Fig. 1. Arid Zones of the Continents and Oceans. 1) Extra-arid and arid ($P/ETP < 0.2$); 2) semiarid ($0.2 < P/ETP < 0.5$); 3) centers of sandy material in deserts at the shores of oceans [34]; 4-7) zones of anomalous positive salinity at the surface of the World ocean, ‰ (4: > 38 , 5: 37-38, 6: 36-37, 7: 35-36); 8) regions with a predominance of atmospheric sediments over evaporation; 9) regions with a predominance of evaporation over quantity of atmospheric sediments; 10) zero isoline for average yearly "sediment-evaporation" difference [2, 3, 5]; 11-13) boundaries (11: arid zones, 12: zones with anomalous positive salinity [10], 13: lithogenesis of arid type in the ocean, identified by A. P. Lisitsyn [13]).

arbitrarily violated (Fig. 1) and, therefore, one of the important climatic criteria for identifying continental arid lithogenesis, the predominance of evaporation over atmospheric sediments, is not met. However, the essence of the matter is not even that the boundaries of arid lithogenesis in the ocean do not everywhere coincide with the zero isoline of the evaporation-sedimentation difference; this was subjected to a valid critique by N. M. Strakhov [21]. The error lies in the very idea of distinguishing arid zones. When trying to show a unity of the climatic types of lithogenesis in the ocean and the continents, A. P. Lisitsyn followed the same criterion as N. M. Strakhov. As a result, he repeated the error of N. M. Strakhov with regard to the formulation of climatic criteria for identifying arid-type lithogenesis. N. M. Strakhov, in creating his own theory, gave attention to the geological essence of the process and was not altogether rigorous in his approach to individual physicogeographic concepts and formulations.

The arid type of lithogenesis, according to the theory of N. M. Strakhov [20], develops only within arid zones of the Earth. However, arid zones are not all regions where the total annual evaporation (evaporation criteria are more properly employed for continents) exceeds the total quantity of atmospheric sediments precipitating annually, but are merely those regions where a similar predominance of evaporation over sediments is very substantial. In physical geography, arid territories are regions with a dry climate controlling the character of the soil and plant cover, the deficiency of internal waters and the regimes of such waters, the character of settlements, the types of economy, etc. Aridity is defined by climatic statistical indices. These include such widely known indices of aridity as that of De Martonne: $i_a = P/(T + 10)$; Keppen: $i_a = 8P/(5T + 120)$, $i_a = 2P/(T + 33)$, and $i_a = P/(T + 7)$; Stentz: $i_a = E/P$; Thorntweite: $i_a = 100 d/n$, and, finally, M. I. Budyko: $i_a = R_0/Lr$, where i_a is the index of aridity; P is the annual total of sediments; T is the average yearly temperature; E is the evaporation; d is the humidity deficit (total monthly differences between P and the total E for those months when the norm for sediments was less than the norm for total evaporation); n is the sum of the monthly values for total E ; R_0 is the radiation balance for a humid surface; and Lr is the latent heat of evaporation [4]. In 1977, UNESCO put together a new map of arid territories at a scale of 1:25,000,000 in order to unify the climatic criteria for identifying arid territories and in order to establish individual boundaries for global arid territories [30]. The ratio of the average yearly quantity of sediments P to the potential evapotranspiration ETP over the same period was used as basis for distinguishing regions with various degrees of aridity. Values for this aridity index were calculated for 1600 stations.

Four types of arid territories were distinguished in all:

1. Superarid ($P/ETP < 0.03$). Characteristically deserts; rain very light and occasional; identical probability of rain over the entire year; long-lived vegetation absent except for sparse shrubs in river beds; ephemerals can develop during favorable years; pasture land and cultivatable land absent; intra-year variation in precipitation of sediments is 100%.

2. Arid ($0.03 < P/ETP < 0.2$). Semidesert; vegetation sparse and consisting of shrubs; nomadic cattle raising; the quantity of sediments varies from 80–150 to 200–300 mm per year; the intrayear variation in precipitation of sediments equals 50–100%.

3. Semiarid ($0.20 < P/ETP < 0.50$). Dry steppes and savannas. The following zones can be distinguished with respect to quantity of sediments: a) from 300–400 to 700–800 mm/yr in regions with maximum rainfall in the summer, and b) from 200–250 to 450–500 mm/yr in regions with winter rains (tropical latitudes of the Mediterranean); intrayear variation in precipitation of sediments is 25–50%.

4. Subhumid ($0.50 < P/ETP < 0.75$). Tropical savannas, mediterranean forest, chernozem steppes; agriculture is usually practiced as in the humid zone: the variation in sediment precipitation is less than 25% within a year.

From the classification presented, it follows that all of the regions with $P/ETP > 0.75$ belong to the humid zone, including those areas where the total annual evaporation predominates over the annual quantity of sediments but where $0.75 < P/ETP < 1.0$. If the arid type of lithogenesis of N. M. Strakhov is strictly correlated with physicogeographical arid zones, then it becomes apparent that the arid type of lithogenesis on continents occurs only in superarid, arid, and semiarid regions (see Fig. 1). A quantitative climatic criterion for distinguishing zones of arid and humid lithogenesis is $P/ETP = 0.5$.

If an improved climatic criterion for the continental arid type of lithogenesis (that is to say the criterion which underlies the distinction between zones of arid lithogenesis in the theory of N. M. Strakhov) is applied to the ocean (this is necessary if one adheres to the conception of A. P. Lisitsyn concerning the identity of physicogeographic criteria for distinguishing arid zones in the ocean and on the continents), the arid zones in the ocean involve additional features and their areas are substantially curtailed (see Fig. 1). An uninterrupted band of arid zone is preserved only in the Northern Atlantic. In the Southern Atlantic and in the Indian and Pacific oceans, the arid zones are belts extending more or less in a latitudinal direction from the western (arid) coasts of the continents in the oceanic side. Moreover, there is an arid zone spatially unrelated to the continents extending along a latitudinal direction in the northern Pacific Ocean.

Aridity of climate on dry land is clearly expressed in the character of the landscape: in the arid zones of all the continents, only desert, semidesert, and steppe landscapes are abundant. The presence of one or another particular landscape is closely linked with the degree of climatic aridity: deserts, arid lands (semideserts and semiarid lands) and dry steppes or savannas correspond to superarid territories. It is different with the situation in the ocean, where arid zones distinguished according to the continental climatic criterion do not have such clear landscape markers. Even elevated salinity of surface waters, which is a reflection of the aridity of the climate according to A. P. Lisitsyn [13], is usually either completely unconnected with arid zones or is located within the boundaries of an arid zone but does not have a clear correlation with the degree of climatic aridity. Actually, zones of maximal salinity located within tropical regions of each ocean (see Fig. 1) or even within the Northern hemisphere, partially coincide with arid zones, although not always with maximally arid zones (for example, in the northern portion of the Pacific Ocean). In the southern hemisphere, regions of maximal salinity in all of the oceans are located within a humid zone. At the same time, all of the zones of anomalous positive salinity (an exception is the maximum in the Southern Atlantic at the coast of South America) clearly coincide with the halistatic regions of the oceanic tropical zones.

This is in complete agreement with fundamental patterns of distribution for salinity fields on the ocean's surface, according to which "in addition to the difference between evaporation and sediments, the thawing of glaciers and river flow, a field of salinity is formed to a significant degree under the influence of the circulation of waters." Due to the return of waters in macrocirculating systems, a field of salinity can be represented by concentric equisalinity lines resembling the elliptical in form as a result of the extension of natural zones along the latitudinal. In the central areas of such regions (simply halystases), positive anomalies of salinity occur. The salinities at the eastern shores of the oceans are lower than at the western shores as a result of the fact that, along the western shores of the oceans, water is transported from tropical regions where the salinity is elevated (the salinity maximum in the Southern Atlantic not coinciding with the center of the halystase is precisely connected with this). Waters with lower salinities from the temperate latitudes are transported along the eastern shores. Therefore, positive anomalies gradually pass through zero and become "negative" with increasing distance from the central regions of elevated salinity to the continents [19, p. 188].*

Thus, the transference of continental climatic criteria to the ocean allows us to distinguish arid zones in which there are neither characteristic (even if specific for the ocean) landscapes allowing them to be distinguished from humid zones nor special sediment types. This was demonstrated satisfactorily by N. M. Strakhov [21-23]; therefore it will not be discussed here. It needs merely to be emphasized that since the "arid" zones distinguished by A. P. Lisitsyn go far beyond the actual boundaries of arid zones ($P/ETP < 0.5$) and encompass large areas of humid zones, the artificiality of identifying specific oceanic deposits which supposedly characterize arid zones and arid zones only becomes still more apparent. Indeed, untypical oceanic deposits are widely distributed in humid zones and in actual arid zones and the fundamental factor controlling their distribution on the ocean bottom is the hydrodynamic regime of the water masses. This was also satisfactorily demonstrated in the reports of N. M. Strakhov [24-26].

The question arises as to whether or not one should distinguish arid zones in the ocean in this case. Apparently such distinctions should be made; but they have significance only for the near-shore zones of the shelf, since one is dealing here with sediment formation on the periphery of a continental block, the type of area for which N. M. Strakhov developed the theory of climatic types of lithogenesis. "The actual signs of aridity are only at the shore: here lagoons and bays occur where chemogenic sediments accumulate: carbonate oolites, lithifacts, and aragonite in the form of needles. Locally, the chemogenic process will have proceeded much further and will have reached the stages of dolomite formation, precipitation of gypsum, and even the more soluble salts up to NaCl (for example, in the sebka in the Persian Gulf, the lowlands of the Sath Peninsula in Western India, in the Bokano de Virilla Lagoon on the coast of Peru, and the Kurong Bay in Australia, etc). At these localities, the very process characteristic of arid lithogenesis is actually realized: the chemical precipitation of salts beginning with the least soluble CaCO_3 and gradually encompassing all of the more soluble salts. But beyond a narrow peripheral margin unrepresentable on the scale of the map, all of the signs of chemical precipitation of salts, including the least soluble of the salts, CaCO_3 , disappear; the authigenesis takes on the usual oceanic character and an arid zone cannot be objectively distinguished in the ocean sediments" [21, p. 21]. Finally, questions concerning sediment formation on the shelf require a deeper and more careful consideration and the citation mentioned concentrates only upon the primary concept involved in nearshore-shelf sedimentogenesis, climatic types of lithogenesis do exist (at least the arid and humid types) and they are most clearly expressed in the nearshore zone, including shallows, bays, lagoons, and inland seas. In this connection, we are astonished at the appearance of a series of reports on nearshore-shelf sedimentogenesis [8, 9] in which the authors attempt to portray themselves as the originators of a concept of climatic types of lithogenesis on the shelf (so that the term lithogenesis is replaced by morpholithogenesis, glacial type, polar; and the humid zone is replaced by humid zone of temperate latitudes and humid

*Expressions presented in brackets and also set off by spacings were provided by V. P. Vasil'ev.

tropical zone, etc. All of this "new theory" does not represent a change in essence and repeats the theory of N. M. Strakhov while its authors pretend to have the role of originators.

Quantity of Eolian Material Entering the Ocean

One of the arguments in favor of distinguishing an arid-type lithogenesis in the ocean concerns an estimate of the quantity of eolian material entering the ocean. A. P. Lisitsyn [13] calculated that 1.6 billion tons of sedimentary material enter the arid zones of the ocean annually. He found that the pelagic portion of the 18.53 billion tons of fluvial material entering the ocean annually amounts to only 7.7%; the remaining 92.3% settles out on the shelf, near the coasts, and at the margins of seas. Eolian and glacial material, according to the theory of A. P. Lisitsyn [14], is totally drawn to the pelagic regions of the oceans. As a result, the quantity of fluviogenic (1.7 billion tons), eolian (1.6 billion tons), and glacial (1.5 billion tons)* material annually reaching the pelagic areas of the world ocean are entirely comparable. This is one of the chief arguments for distinguishing climatic types of lithogenesis in the ocean. Thus, an exact estimate of the quantity of eolian material entering the world ocean has major significance for the theory of oceanic sedimentogenesis.

Before going on to a critical analysis of the estimate of eolian material obtained (1.6 billion tons/yr), however, we will discuss the problems involved with the zonality of eolian processes. Until recently, it was believed that eolian processes were presented only in arid zones. The investigations of recent years have shown that this is not the case. Wind erosion (deflation), having maximal intensity in desert regions, is widely distributed in other climatic zones. The intensification of wind erosion in humid regions is facilitated by the progressive development of land which is evident in the cutting of forests and plowing of land under agricultural cultivation. From the data presented in Table 1, it is evident that areas of land being worked at present are comparable to the areas of the desert regions. Since the former are located, as a rule, in humid regions, wind erosion (facilitated by the removal of vegetative cover) extends beyond the arid zones into the humid zones. It is possible to make inferences concerning the scales of wind erosion in humid regions on the basis of the following data. As a result of the elevated wind activity during the summer and early spring in the period of 1968-1969, a layer of chernozem soil together with snow in the Rostovskoi region and the Krasnodarsk border was transported to the ice cover of the Azov Sea. In the spring, samples of snow were collected and the total quantity of eolian material entering the water area of the Azov Sea was determined to be 50 million tons. In 1959, approximately 41 million tons of terrigenous material was transported to the Azov Sea by hurricane winds [29].

At the 17th Annual Binghamton Geomorphological Symposium, a symposium concerned with eolian processes, it was pointed out that wind erosion has a global presence not only on Earth (from the equator to the poles) but also on other planets of the solar system [31]. An important conclusion follows from this: wind erosion is not a narrow zonal process manifesting only in the arid zones of the Earth but is a phenomenon of planetary scale. Therefore, terrigenous material of eolian origin cannot serve as a criterion for distinguishing zones of arid-type lithogenesis. In arid zones, wind erosion manifests at maximum scales as a consequence of the anomalous dryness of climate and the paucity of fluvial deposits.

A second question concerning the zonality of eolian processes is the zonality of wind transport. Despite predominantly latitudinal wind transport, processes involving exchange of air masses in the meridional direction, up to the scale of air exchange between the Northern and Southern hemispheres [28], are widespread on our planet. Precisely because of the processes of meridional exchange of air masses, eolian material from the desert regions enters various climatic zones as far as the poles [7, 36-38]. This is still another indication of the global nature of the transport and deposition of eolian material, evidence that these processes cannot be considered as reliable indicators of arid-type lithogenesis. Moreover, the complexity (and, in part, impossibility) of identifying an eolian and only eolian genesis for detrital grains is yet another important argument against using this criterion for identifying arid conditions of sedimentation. The so-called desert varnish which clearly characterizes quartz grains from desert regions is found on grains of silic minerals which have entered the ocean from lateritic weathered crusts in the equatorial humid zone.

In conclusion, a discussion of the problems of zonality in the transport and sedimentation of eolian material needs to take into account what A. P. Lisitsyn wrote concerning the predominant deposition of eolian material arriving from the arid zones of the continents in the humid zones of the ocean: "Another important conclusion is the fact that the major portion of this (eolian — V. V.) material (9/10) is precipitated not within arid zones but within the noted bound-

*Estimates of A. P. Lisitsyn [13, 14]. New data has now been obtained by the author for steady fluvial (19.288 billion tons/yr) and glacial (0.373 billion tons/yr) discharges. Only 30% (0.112 billion tons/yr) of iceberg material reaches the pelagic regions of the ocean.

TABLE 1. Total Balance for Lands of the World [12]

Land resource	Total area, millions of Ha	Percentage of area		
		land sources	dry land as a whole	surface of planet earth
Land resource as a whole	13 392	100,0	89,8	26,2
Productive land	8 570	64,0	57,5	16,8
Cultivated lands	4 559	34,0	30,6	8,9
Of these:				
plowed fields	1 356	10,1	9,1	2,6
gardens and plantations	93	0,7	0,6	0,2
meadows and plantations	3 110	23,2	20,9	6,1
forests and brushlands	4 011	30,0	26,9	7,9
Low-productivity lands	2 818	21,0	18,9	5,5
Of these:				
lands of populated locality	440	3,2	3,0	0,9
industry and transport,				
lakes, rivers, and dams,	317	2,4	2,1	0,6
tundra, and tundra-forest	734	5,5	4,9	1,4
marshes	400	3,0	2,7	0,8
deserts	925	6,9	6,2	1,8
Nonproductive lands	2 006	15,0	13,4	3,9
Including:				
lands disturbed by man	450	3,4	3,0	0,9
sands and gullies	378	2,8	2,5	0,7
ice and snow fields	1 178	8,8	7,9	2,3
Antarctica	1 523	—	10,2	3,0
Dry lands in general	14 915	—	100,0	29,2
World ocean	36 105	—	—	70,8
Surface of Planet Earth	51 020	—	—	100,0

aries of adjacent humid zones, temperate and equatorial. Thus, arid zones make a certain contribution to the sediment accumulation in humid zones" [13, p. 78]. After this, calculations of eolian material (even approximate) in which the area of arid zones of the ocean are used seem quite illogical.

How was the total quantity of eolian material entering the ocean estimated to equal 1.6 billion tons/yr? "If one takes the average diameter of a particle to be $10\ \mu\text{m}$ (0.01 mm), its weight will equal approximately 10^{-10} g. The rate of fall of particles of such diameter is approximately 0.7 cm/sec, i.e., ash from a column approximately 600 m in height should reach the ground over the course of a day (? — V. V.); this yields 6 g of ash per $1\ \text{m}^2$ (? — V. V.). For a total area of precipitation equaling 175.0 million km^2 (? — V. V.), this yields 1.0–1.1 billion tons of ash per year. If one assumes that 100–200 million tons (? — V. V.) are precipitated into inland water bodies and also into regions of Australia and other areas where dry hazes, occur, we obtain an average figure for the arrival of terrigenous material by the eolian route equaling 1600 million tons per year (? — V. V.)" [13, p. 78]. Commentary, so to speak, would be superfluous. Massive problems exist here. Calculations of the quantity of terrigenous material in arid zones carried out on the basis of a map of absolute masses of terrigenous material in the oceans [14] are convincing with regard to the fact that the estimate obtained significantly exceeds the actual influx of such material. The results of the calculations we performed are shown in Table 2. As is evident from the data presented, the quantity of terrigenous material annually entering arid zones (714.12 million tons) is less than one half of the quantity of eolian material calculated by A. P. Lisitsyn. However, the estimate obtained cannot be considered a global estimate of detrital material of eolian origin entering the oceans for a number of reasons. In the first place, the boundaries of arid zones proposed by A. P. Lisitsyn were used for the calculations; these boundaries, as shown above, do not correspond to actual arid zones of the ocean identified on the basis of generally accepted continental climatic criteria. In the second place, eolian material enters not only arid but also other climatic zones of the ocean, although at smaller scales. In the third place, not all of the terrigenous material accumulating on the bottoms of arid zones of the ocean is of eolian origin. A substantial fraction of the terrigenous material entering arid zones is fluviogenic material which crossed the "barrier" of the precontinental zone of avalanche sedimentation. The only exception is a comparatively small region of the Atlantic Ocean (the "Sea of Darkness") adjacent to the Sahara, where liquid and consequently solid run-off is generally absent. In other regions of the ocean's arid zones, numerous rivers have their discharges, including such large-scale rivers as the Indus, Tigris, Euphrates, Nile, Colorado, Kunene, and Orange. These rivers carry out the primary bulk of terrigenous detrital material to the oceans. Evidence of the significant contribution of fluviogenic material to pelagic regions of the arid zone of the ocean includes, for example, calculations carried out for the southern portion of the Pacific Ocean. Here, the areas of the humid and arid zones of lithogeneous (within the boundaries defined by A. P. Lisitsyn) are roughly comparable. In the pelagic region of the arid zone of the southern portion of the Pacific Ocean, 101 million tons of terrigenous material settles out annually (see Table 2). The solid run-offs from Australia and South America to the Pacific Ocean equal 367 and 689

TABLE 2. Quantity of Terrigenous Material in the Arid Zones of the Ocean Calculated According to Maps of Absolute Mass

Ocean	Hemisphere	Av. of rate of sedimentation, tons/km ² ·yr	Area of ocean bottom with a given rate of sedimentation, km · 10 ⁶	Quantity of terrigenous material, tons · 10 ² /yr
Atlantic	Northern	10	5,63	56,3
		1	11,25	11,25
	Southern	10	6,75	67,5
		3,5	16,87	59,05
		1	3,38	3,38
	Σ	—	43,88	197,48
Indian	Northern	10	2,25	22,5
		1	2,25	2,25
	Southern	10	21,38	213,8
		1	9,00	9,0
	Σ	—	34,88	247,55
Pacific	Northern	10	5,63	56,30
		3,5	31,94	111,79
	Southern	10	6,97	69,70
		3,5	3,38	11,83
		1	14,63	14,63
		0,25	19,34	4,84
	Σ	—	81,89	269,09
	World ocean	—	160,65	714,12

million tons/yr respectively, totally 1056 million tons/yr.* According to the data of A. P. Lisitsyn [14], only 7.7% of the fluvio-genic material reaches the pelagic regions of the ocean. Consequently, more than 81 million tons of fluvial material reaches the pelagic region in the southern portion of the Pacific Ocean. Approximately 40 million tons of this amount arrives at the arid zone. Thus, almost half of the terrigenous material in the arid zone of the southern portion of the Pacific Ocean (40 million tons out of 101 million tons arriving annually) has a fluvio-genic origin.

Having pointed out the overstatement involved in A. P. Lisitsyn's estimate of eolian material arriving to the ocean, let us attempt to calculate the actual value using estimates obtained on the basis of various data for the global release of soil-erosional (mineral) aerosol into the atmosphere and its concentration. Estimates of global release of mineral aerosol into the atmosphere obtained according to various data are presented in Table 3.

Practically all existing estimates of the quantity of mineral substances entering the atmosphere are significantly lower than the estimates put forward by A. P. Lisitsyn. By analyzing the data presented in Table 3, K. Ya. Kondrat'ev et al. [11] suggested assuming the quantity of mineral aerosol annually entering the atmosphere to be 500 million tons by taking into account that estimates with respect to ice fields were underestimated while those based on 15 stations in the USA were overestimated. L. S. Ivlev [6] suggested using an estimate of 960 million tons/yr as closest to the actual.†

In order to distinguish between one or another point of view, we attempted to calculate the average quantity of mineral aerosol annually entering the atmosphere on the basis of existing data on the average yearly concentrations of aerosols and by applying a method of local extrapolation. All of the territories of the planet can be provisionally classified into a number of landscape zones characterized by approximately equal average yearly concentrations of mineral aerosols. Four such zones can be differentiated for dry lands: 1) arid and extra-arid (deserts and semideserts); 2) semi-arid (steppes and savannas); 3) lands used by man within arid and semi-arid zones (plowed lands, gardens, plantations, meadows, pastures, and the lands of population centers, industry, and transport); 4) the remaining portion of dry land (forest, marsh, tundra, and tundra-forest, ice field, snow field, etc). Average yearly concentrations of atmospheric aerosol in each of the identified zones can be assumed on the basis of an analogy with existing values for the territory of the Soviet Union [16]: in the first zone, 125 (in $\mu\text{g}/\text{m}^3$); in the second 75; in the third 35, and in the fourth 5. One can assume an average yearly concentration of aerosol in the atmosphere equal to 5 $\mu\text{g}/\text{m}^3$ for the entire area of the ocean, despite the presence of anomalous zones in regions adjacent to deserts. An analysis of the existing data [6, 11, 17] allows us to include in our calculations only the lower 6-km layer of the troposphere, in which the primary bulk of atmospheric mineral aerosol of terrigenous origin is concentrated. Taking into account the average height of dry land above sea level (875 m [15]), the height of the aerosol-containing layer above dry land will amount to 5.125 km; whereas, it will be 6 km over the ocean. The most representative dimensions of mineral aerosol are 1-10

* Vasil'ev, V. P., "Solid river discharge to the World Ocean," *Litol. Polezn. Iskop.*, No. 6, 9-28 (1987).

† Erroneously attributed this estimate to O. P. Petrenchuk [17], since, for the latter, 920 million tons/yr applied only to soluble substances entering the atmosphere from soils.

TABLE 3. Estimates of the Global Releases of Mineral Aerosol into the Atmosphere [6, 11, 17]

Quantity of mineral aerosol entering the atm. millions of tons/yr.	Source and manner of calc.
1100	Data from 15 stations in the USA on annual ash fall extrapolated to the remaining portion of the planet potentially subject to erosion
500	Conc. of ash taken to be $5 \mu/m^3$ in the first 5-km layer, number of removal cycles in year
500	Extrapolation of estimate of J. Wadley for ash created as a result of natural erosion and erosion caused by agricultural activity within the territory of the USA
250	Extrapolation performed by Z. Peterson and H. Jung, quantity of natural ash and ash formed as a result of agricultural operations, lifted by wind over the USA
100-500	Data of E. Goldberg on the rate of accumulation of eolian material in ice fields and marine sediments
200	Data of G. Robins assuming in the calculations that the concentration of atmospheric ash is a constant
6-600	Scatter in estimates based on various published data collected by S. Jadson
200	Conc. of ash taken to be $10 \mu/m^3$ in a layer for a life times of 3 and 5-30 days respectively
70-100	Data on ash deposits in ice fields
380	Data of O. P. Petrenchuk obtained on the basis of the annual quantity of atmospheric sediments on the Earth equaling $0.5 \cdot 10^{-3} \text{ mm/yr}$, density of sediments $577 \cdot 10^3 \text{ km}^3$, their average mineralization is 6.2 mg/liter and the ratios of primary components: sea salts 23%, soil particles, 26%, sulfur compounds, 51%
9000	

TABLE 4. Entrance of Terrigenous Mineral Aerosol to the Atmosphere

Landscape zone	Area, millions of km^2	Volume of aerosol-containing layer of atm., millions km^3	Av. yearly concn. of aerosol, tons/km	Quantity of aerosol over 1 cycle a year, millions of tons	Quantity of aerosol over a year, millions of tons
Deserts and semideserts	27.5*	140.9	0.125	17.6	369.9
Steppes and savannas	21.2*	108.7	0.075	8.2	171.2
Lands used by man within the arid and semiarid zones	10.6†	54.3	0.035	1.9	39.9
Remaining portion of dry	89.9	460.7	0.005	2.3	48.4
World ocean	361.0	2166.0	0.005	10.8	194.9
Σ	—	—	—	—	824.3

*Data of P. Meigs [18]

†Data obtained by subtracting from the total area of land used by man (see Table 1) areas used in semiarid and arid territories; 9.3 million km^2 of the land in such territories is not used.

μm , with an average of $5 \mu\text{m}$ [11]. The rate of fall of particles with dimensions of $5 \mu\text{m}$ is 0.35 cm/sec [27]. Consequently, all of the aerosol from a layer of atmosphere with a height of 5.125 km settles out within approximately 17 days; the aerosol over the ocean settles out by 20 days. Over a year, there will be 21 cycles of removal of atmospheric aerosol over dry land and 18 over the ocean. On the basis of the considerations mentioned, we calculated the total quantity of aerosol annually entering the atmosphere from dry land (Table 4).

The estimate of atmospheric mineral aerosol obtained ($824.3 \text{ million tons/yr}$) is still only approximate, but it differs negligibly from the estimates assumed by many specialists studying atmospheric aerosol [6, 11]. The methodology involved in its calculation, based upon the results of regular naturalistic observations of the concentrations of atmospheric aerosol and making use of a method of local extrapolation of the evidence observed, allows us to suggest that this estimate is close to the actual value.

TABLE 5. Arrival of Atmospheric Mineral Aerosol to Various Regions of the World Ocean [32]

Region of the world ocean	Quantity of eolian material	
	10^{-6} g/cm ² ·yr	10^{12} g/yr
N. Atlantic from the zone of tradewinds	82	12
N. Atlantic in the zone of tradewinds	—	100—400
S. Atlantic	85	18—37
Pacific Ocean	37	66
Indian Ocean	450	336
World ocean in general (minimum—maximum)	—	532—851

In order to obtain an average estimate of the eolian material entering the ocean, it is entirely permissible to assume a uniform distribution of aerosol precipitating over the surface of the plant. Consequently, 583.2 million tons out of 824.3 million tons of eolian material enters the oceans annually and 241.1 million tons arrives on dry land.

It is necessary to keep in mind that the value obtained for the quantity of eolian material (583.2 million tons) is an average value fairly close to the computed estimate of J. Prospero (Table 5). The distribution of this material over the bottom area is extremely irregular. Computed data on the arrival of eolian material to various regions of the world ocean is presented in Table 5 [32]. The largest-scale centers of eolian sedimentation are concentrated in the tropical zone of the ocean, in areas adjacent to the deserts of the continents. One of the most studied of such areas is the tropical zone of the Northern Atlantic between 10 and 25°N latitude. The annual transport of ash through this zone from the Sahara in the direction of Central America amounts to 25–37 million tons according to an earlier estimate [33] and 275 million tons according to a latter estimate, 70% of this 275 million tons (193 million tons) is seen as settling to the surface of the ocean during the crossing of the first 2000 km (up to 34°W longitude); of the 82 million tons remaining in the current, 32 million tons is believed to fall out in an area between 34–60°W longitude, while 50 million tons reaches Barbados [35]. However, the latter estimate is apparently too high. The actual quantity of terrigenous material (though not eolian only) annually accumulated in this zone amounts to approximately 68 million tons (see Table 2). The exaggeration in the estimate of the quantity settling out along the path of transport of the eolian material is apparently connected with an erroneous interpretation of the gradual fall in the aerosol concentration along the path of predominant transport only as a consequence of precipitation of the airborne suspension. Simultaneously with transport in the latitudinal direction, the airborne suspension is moved in a meridional direction and is also diffused into the overlying layers of atmosphere, which naturally also leads to a lowering of the concentration of aerosol at observation stations located along the path of predominant transport. This is confirmed by observations in Great Britain, where eolian ash is precipitated from the Africa continent during periods of wind activity in the Sahara [36].

Observations of mineral aerosols from other regions are clearly insufficient. Thus, there is data that approximately 0.5 million tons of mineral ash were transported to the Arctic (the region of Alaska) from the Asiatic Gobi and Takla-Makan deserts [11]. However, the results of similar unsystematic observations can not be relied upon as a basis of obtaining concrete, even if approximate estimates of the quantity of eolian material entering the Arctic region.

In addition to the finely dispersed tropical aerosol predominately entering the deep-water region of the ocean (we have estimated the quantity of this to be 583.2 million tons/yr), large volumes of sand and silt enter the nearshore zone and the shelf as a result of local wind transport from sandy deserts located at the shores of the ocean. Estimates obtained for several regions indicate the scale of this process. N. A. Aibulatov and V. V. Serova [1] found that throughout the coasts of Libya and Tunis (the length of coastline is 1100 km) approximately 5.5 million tons/yr of eolian material is transported to the Mediterranean Sea by dust storms alone. It has been found that $5-8.5(13?) \cdot 10^6$ m³ of sand arrives at the shelf of the Atlantic Ocean from the Sahara annually [34]. The report cited includes a map of the distribution of eolian sands of the world from which turbidites are formed on the submarine continental margin. The largest-scale centers of influx of sandy eolian material to the shelf are concentrated in the sandy deserts at the shores of the oceans (see figure): 1) the Sahara (Northern Africa); 2) the Namib (Southern Africa), 3) the desert of Rub al-Khali (the coast of the Persian Gulf), 4) the deserts of Peru and Chile, 5) the deserts of California, 6) the deserts of western Australia. By knowing the patterns of transport of sandy material by wind, one can calculate the total quantity of such material arriving at the shelf.

The sands begin their movement under the influence of winds with minimum velocities of 5–6 m/sec. Various formulas and curves exist which make it possible for one to determine the quantity of sand winnowed across one unit of length over a period of time for a specific wind strength [18]. We used the results of S. P. Rat'kovskii's naturalistic observations of winnowed sands [18] for our calculations. This was connected with the fact that the estimated quantity

TABLE 6. Arrival of Sandy Material to the Shelf from Sandy Deserts

Region	Extent of sandy coasts	Direction of wind for which transport of sand to the ocean exists	Wind velocity, m/sec	Recurrence per year, %	Duration in portion of year	Quantity of sand arriving at the shelf, m. tons/yr
Sahara	600	NE, E, +SE	6,9 10,4 15,6	24,83 7,33 0,58	0,2483 0,0733 0,0058	15,660 15,025 4,725
Σ	—	—	—	—	—	35,410
Namib	1400	NE, E, +SE	6,9 10,4 15,6	8,33 2,50 0,75	0,0833 0,025 0,0075	12,259 11,958 14,257
Σ	—	—	—	—	—	38,474
Shore of Persides Bay	300	S, E, SE	6,9 10,4 15,6	10,33 1,92 0,08	0,1033 0,0192 0,0008	3,257 1,968 0,326
Σ	—	—	—	—	—	5,551
California	500	NE, E, N	6,9 10,4 15,6	10,00 0,92 0,08	0,1 0,0092 0,0008	5,256 1,571 0,543
Σ	—	—	—	—	—	7,370
South America	3000	E, NE, SE	6,9 10,4	26,99 7,00	0,2699 0,07	42,558 35,872
Σ	—	—	—	—	—	78,430
Australia, north	400	S, E, SE	6,9 10,4 15,6	20,75 4,08 0,08	0,2075 0,0408 0,0008	8,725 5,576 0,434
south	400	NE, E, SE	6,9 10,4 15,6	16,00 3,00 0,08	0,16 0,03 0,0008	6,728 4,100 0,434
Σ	—	—	—	—	—	25,997
Total	—	—	—	—	—	191,232

of sand arriving at the shelf of the Sahara as calculated according to the data of S. P. Rat'kovskii [18] is in good agreement with the actual estimates obtained on the basis of a direct study of the areas of distribution and the thicknesses of sands on the shelf and continental slope of the Sahara [34]. As a result of extrapolation, we obtained from the data of S. P. Rat'kovskii that 105.12 thousand tons of sand are moved through a one km unit of length per year for an average wind strength of 6.9 m/sec; for an average wind strength of 10.4 m/sec, 341.64 thousand tons/yr are moved. Rose diagrams of the winds were used from the Atlas of Oceans [2, 3] for the computed regions. The results of the calculations performed are presented in Table 6.

The sandy material entering the shelf from the largest desert regions of the world amounts to 191.2 million tons/yr. Taking this material into account, the total quantity of eolian flow of undissolved mineral substances from dry lands to the ocean is estimated to be 774.4 million tons/yr. Thus, the eolian material (0.8 billion tons) is not at all comparable to the fluviogenic material 18.5 billion tons), neither with respect to the total contribution to oceanic sedimentation nor with respect to the contribution to sediment formation in deep-water regions (0.6 and 1.7 billion tons) respectively.

The material presented, reasonable on the basis of generally accepted climatic criteria for aridity used to establish new boundaries of arid zones in the ocean and to obtain new estimates of the contribution of eolian material to oceanic sedimentation, is, from our point of view, still another indication of the lack of grounds for identifying arid-type lithogenesis in the ocean.

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MINERALOGY AND FORMATION OF THE OXIDE AND HYDROXIDE FORMS OF IRON AND MANGANESE IN THE RIFT ZONE OF THE RED SEA

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On the basis of a detailed investigation of the oxide and hydroxide compounds of iron and manganese in the ore material of the sediments of the Atlantis II and Tethys Deeps (Red Sea), we identified the principal paths of formation and transformation of the mineral phases and suggest an important scheme of mineral-forming processes controlling the actual physicochemical conditions of the environment.

In the first part of this report, we characterized the complex of iron and manganese oxide compounds occurring in the hydrothermal-sedimentary deposits of the Atlantis II and Tethys Deeps.

The compositions of minerals and their paragenetic associations and peculiarities of distribution in sediments reflect complex processes of mineral formation requiring interpretation and discovery of the actual factors controlling the formation of one or another mineral phase, the structural-crystallochemical peculiarities of the phases, and their parageneses. The substantial differences in the mineral associations occurring in the Atlantis II and Tethys Deeps make separate discussions advisable for the conditions and mechanisms of mineral formation in each deep.

The Atlantis II Deep

Within the Red-sea rift, it is precisely in this deep that the ore-forming process manifests with maximum activity. The hydrothermal source here has been in operation with varying intensity over the last 20-25 thousand years and the deposits formed during this process represent an economically valuable ore accumulation. The structure of the section of sedimentary strata and its general mineralogical-chemical features were discussed in a series of reports [1, 5, 8, 14, 16, etc.] and a scheme of the geochemical processes involved in the sedimentation was presented in [4].

Let us recall that the Atlantis II Deep (70 km² in area) is filled with dense, highly mineralized thermal brines with a thickness on the order of 170 m and with a clearly expressed vertical stratification. The lower, thickest layer has a temperature of 62-65°C, a salinity of up to 320 ‰, and a pH of 5.5-5.6; it is entirely devoid of oxygen. Along a clearly expressed boundary above this layer, changes in all of the parameters of the water mass occur. The temperature falls to 51°C, the salinity becomes 153 ‰, the pH is 5.9, and a small quantity of oxygen appears (0.05-0.06 mg/l). This layer, with a thickness on the order of 30 m, passes into normal sea water through an intervening horizon of approximately the same thickness [13, 18].

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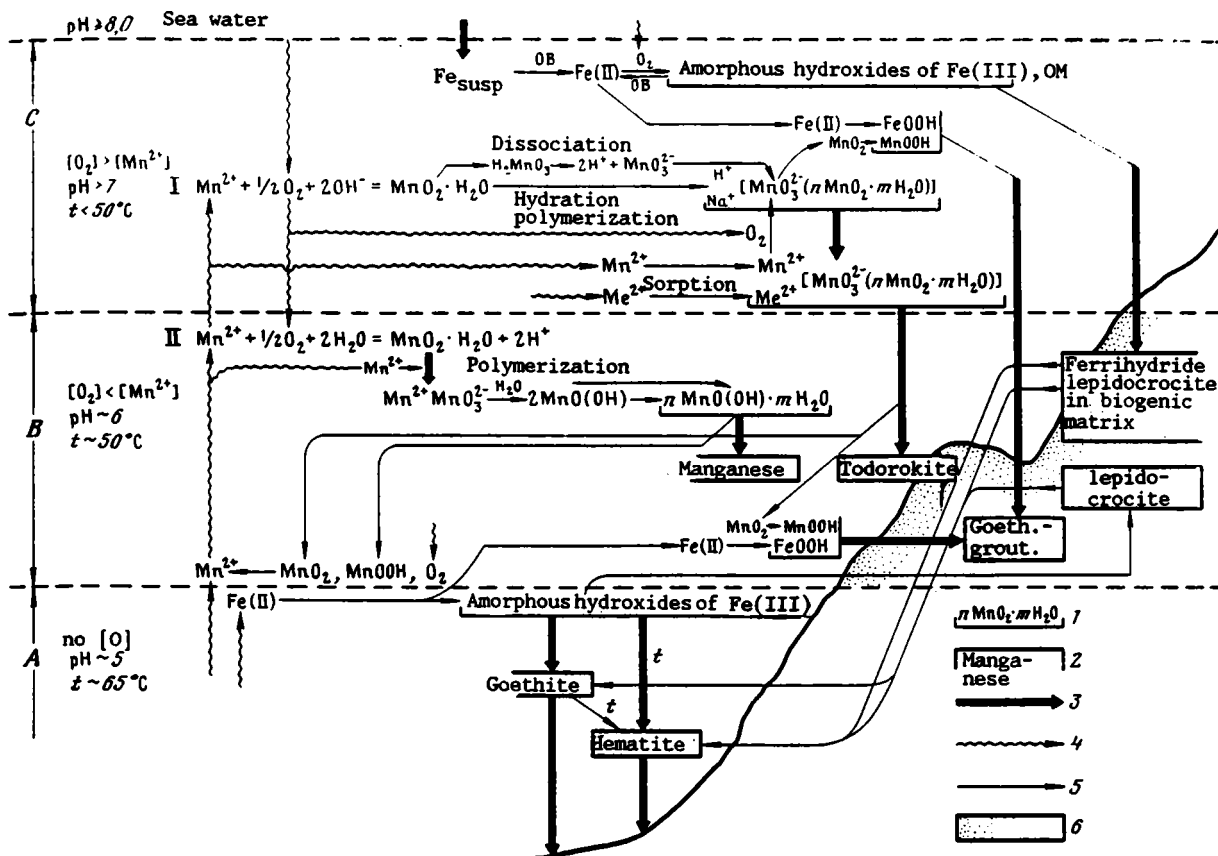


Fig. 1. Diagram of iron—manganese mineral formation in the Atlantis II Deep (Red Sea) A, B, and C) layers of brine strata (A: lower, B: upper, C: transitional to sea water); I, II) upper and lower zones of oxidation respectively: 1) solid phase of suspension; 2) mineral species; 3) sedimentation with parallel mineralization (coagulation, dehydration, crystallization); 4) migration in solution; 5) transformation of solid phases of suspension and sediments; 6) region deposits of manganese-ore sediments.

The distinguishing feature in the chemical compositions of the brines when compared with sea waters consists in the high contents of such elements as Cl, Na, Ca, K, and Si, the sharply elevated concentrations of ore components (Fe, Mn, Zn, Pb, and Cu) and also the low (relative to sea water) containing Mg and SO_4 . Free H_2S was observed in any of the layers of the brine stratum [2, 3].

As was noted in Part 1, the oxide forms of iron and manganese occurring in the ore stratum in the Atlantis II Deep are characterized by a great variety of mineral forms, morphological and geochemical peculiarities, and various degrees of crystallization, that, taking into consideration their localization, definitely indicate a spatial differentiation in the conditions of mineral formation, both in the contemporary stage and in the period corresponding to the formation of the manganese-ore interlayers occurring within the sedimentary section. This situation allows us to outline a unified, principal scheme for the processes involved in the formation of an complex combination of oxide compounds of iron and manganese on the basis of the published data on the structure of the stratum of brines filling the deep and for their physicochemical characteristics. The diagram presented in Fig. 1 serves as the basis for further interpretation of the mineral forming mechanisms. A very important addition to the scheme we have put together is the data on the distribution of iron and manganese in the brine stratum from the contact with bottom sediments to the boundary with sea water (Fig. 2). The observed character of the distribution of major ore components entering into the composition of the thermal springs in the forms of Fe(II) and Mn(II) are directly connected with the formation of the solid-phases and, most importantly, the oxides of their compounds and demonstrate the difference in the behaviors of iron and manganese.

Formation of Oxides and Hydroxides of Iron. It is clearly evident on the graph (see Fig. 2) that an abrupt change (jump) in the contents of iron in the brine stratum occurs at the boundary of the lower layer A with the above-lying horizon B. This fall is due to the massive transition of dissolved iron to solid phases in a zone where, as pointed out earlier, oxygen is present. The significant increase in rust-brown suspended material noted by M. Hartman [17] (material which, according to his data, is entirely x-ray amorphous) is a direct confirmation of the formation of the

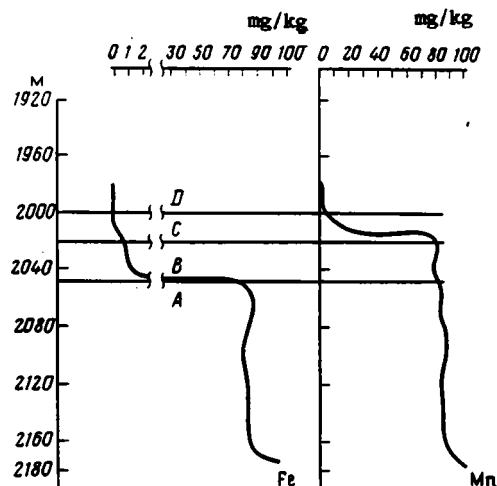


Fig. 2. Distribution of Fe and Mn in the stratum of brines in the Atlantis II Deep [2], A, B) lower and upper layers of brines respectively; C) layer transitional to sea water; D) sea water.

groundmass of iron hydroxides at the boundary of the two layers of the brine stratum. However, N. Holm et al. [19] found the mineral phase βFeOOH (akaganeite, the nature of this phase and the conditions of its synthesis are fairly well studied and are covered in [10]) in the composition of the suspended material. The majority of investigators believe that the presence of chlorine (or fluorine anions) and also a neutral reaction of the environment are necessary conditions for the formation of the βFeOOH phase. These conditions are fully realized within the Atlantis II Deep. Akaganeite, for a time the natural crystallized phase of Fe(III), is found in small quantities with suspensions from the brines of the Atlantis II Deep. At the same time, this mineral has not been found, either by us or previous investigators, in the sediments. Considering the metastability of the βFeOOH phase, one can assume a rapid transformation of akaganeite to more stable crystalline phases (goethite, hematite). Another possible cause of the absence of akaganeite in the ore material of the sediments could be its destruction as a result of the removal (leaching) of chlorine from the structure of the freshly formed mineral as the sample was washed with water for the removal of easily dissolved salts. The breakdown of akaganeite when chlorine is removed from it was demonstrated experimentally [10].

Two major mineral associations of Fe oxides can be identified within the ore stratum of the Atlantis II Deep: goethite-hematite, characteristic of the iron-ore deposits of all the lithological-facies zones and ferrihydrite-lepidocrocite, coinciding with interlayers enriched in manganese. Small quantities of ferrihydrite are also found in iron-ore sediments, mostly in the upper horizons of the sections studied [6].

It was shown above that the groundmass of oxidized iron arises at the boundary of the two layers (A and B) of the brine stratum (see Figs. 1 and 2); consequently, the amorphous hydroxides formed here in particular are important for the formation of a major portion of the goethite and hematite constituting the ore material of the sediments.

Goethite, as is well known, forms over a wide range of conditions in comparison with other iron minerals; however, numerous experiments on the synthesis of ferruginous phases demonstrated that high concentrations of Fe^{2+} in the solution facilitate its formation in the presence of small concentrations of oxygen and also relatively low pH values for the medium [9]. The region of formation of the groundmass of iron hydroxides corresponds to precisely these conditions. The regular increase in the crystallization and structural ordering of the goethite from top to bottom along the section of the ore stratum confirms the formation of a major portion of the goethite as a result of a recrystallization of an amorphous phase. Thinly scaled aggregate of particles with hexagonal packing of anions would be formed as a consequences of this.

The other possible path of formation of goethite is connected with the transformation of lepidocrocite. Since a cubic packing of anions is realized in the structure of the latter, this process is carried out as a result of a solution-precipitation reaction with the formation of crystals of the more stable modification αFeOOH . In [11], it was shown that elevated temperatures, high dispersion of the particles of the mineral and weak crystallization facilitate the transition of lepidocrocite to goethite. It can be assumed that the absence of lepidocrocite to goethite. It can be assumed that the absence of lepidocrocite in the iron-ore sediments is connected with its conversion to goethite at elevated temperatures ($>65^\circ\text{C}$).

In contrast to goethite, higher temperatures are usually required in hematite for the crystallization of amorphous hydroxides. The character of the localization of ferruginous minerals over the area of the deep is in complete accord with this condition. Thus, the maximum quantities of well crystallized hematite in the form of characteristic hexahedrons coincides with regions located in direct proximity to sites of thermal-spring discharge. In the sections studied, the total content of hematite is also significantly higher in the sediments at Site 1905(5), located near the mouth of the sources, than in the core of at Site 1905(4) [6].

The presence of another morphological variety of hematite (thinly scaled aggregates) in the sediments of both sections is probably due to the transformation of ferrihydrite to hematite. This process is fairly well investigated and has been confirmed experimentally [7]. The relative ease associated with the transformation of ferrihydrite to hematite is connected with the similarity between their crystal structures. A packing of anions positioned in a hexagonal motif in which the octahedral positions are replaced by Fe^{3+} cations constitutes the basis of both minerals. In contrast to hematite Fe_2O_3 , a portion of the oxygen anions in ferrihydrite are replaced by OH and H_2O . This results in an additional deficit of Fe^{3+} cations in the octahedral positions, cations which are irregularly distributed in the structure of ferrihydrite for this reason. Dehydration of ferrihydrite particles can fairly easily transform the structure of ferrihydrite to that of hematite while conserving the high dispersion of the particles of the mineral.

It is important to note that ferrihydrite in iron-ore sediments is preserved only in the upper portions of the sections (in the core of 1905(5), it is preserved in the surficial horizon; in the core of 1905(4), it is preserved to a depth of 2.5 m) [6]. It can be assumed that the major portion of the mineral is transformed into hematite during the aging of the sediment. Under conditions of elevated temperature, the formation of hematite could occur as a result of the transformation of hematite (see Fig. 1).

In general, the irregular distribution of goethite and hematite along the vertical section of the ore stratum and also the differences in morphological aspect of both goethite and hematite reflect different paths associated with their formation, the chief among them being those discussed above.

Ferrihydrite, occurring both in iron-ore deposits and in interlayers enriched in manganese, has a clearly expressed bacteriallike form of particle that can be considered evidence of the active role of microbiological processes in the formation of this mineral. Apparently, the most favorable environment for active microbiological oxidative—reductive reworking of the ferruginous suspension is the brine stratum C transitional to sea water, which is a gradient zone with a significant decrease in density and an increase in the content of oxygen (see Fig. 1).

Consequently, the conditions for the formation of amorphous hydroxides of iron transformed into goethite and hematite on the one hand and, into ferrihydrite on the other hand, are spatially separated. The sources of the iron are also different; in the first case amorphous hydroxides are formed during the oxidation of the Fe(II) entering into the composition of the thermal springs; in the second case, the iron is a result of a conversion of the ferruginous suspension from sea water.

As noted in Part I [6], two morphological (and genetic) varieties of lepidocrocite can be found in the manganese-ore horizons. One, similar to ferrihydrite, has a bacteriallike form of particle, i.e., develops in a biogenic matrix as a result of the same processes and under the same conditions as ferrihydrite. Abiogenic lepidocrocite is probably formed as a result of the oxidation of Fe(II) in the border zone of the brines between layers A and B. It can be assumed that the widespread occurrence of the hydrated forms of manganese dioxides in the manganese-ore interlayers and also the presence of amorphous SiO_2 facilitate the preservation of the metastable hydroxide phases of iron, ferrihydrite and lepidocrocite in the sediment.

It should be noted that despite the widespread occurrence of oxide and hydroxides of iron in various natural environments, many features associated with the processes of their formation and transformation have been investigated in insufficient detail. In part, this is connected with the absence of experimental studies which can be reliably extrapolated to natural processes. In addition, the same ferruginous mineral could be formed under a fairly wide range of physicochemical environments; this makes such minerals significantly less informative for interpreting the conditions of mineral formation when compared to complexes of the oxide minerals of manganese.

Formation of Oxides and Hydroxides of Manganese. The behavior of hydrothermal manganese in the brine stratum within the Atlantis II Deep is substantially different from the behavior of iron.

Because of a higher oxidation potential than that found in iron, the transfer of hydrothermal Mn(II) from solution to the solid-phase compounds of Mn(IV) takes place in the layer of brine where the oxygen of sea water actively penetrates. The process of bulk oxidation of Mn^{2+} is reflected on the graph (see Fig. 2) by the sharp fall (jump) in its content at the layer C transitional to normal sea water. According to the data presented in [17], it is precisely in this layer that one can see a significant quantity of brown suspended material consisting of amorphous Mn hydroxides.

Sinking down to the brine stratum and reaching the lower layer A, where oxygen is completely absent, the particles of hydrated dioxides are reduced by dissolved Fe(II) and manganese again passes into solution. This process

impedes the precipitation of the oxide forms of manganese into the sediment in the region where the thick brine stratum occurs and favors a high concentration (80-90 mg/liter) of elements in solution. This concentration is approximately 20 thousand times higher than the average concentrations of manganese in sea water [2]. A natural consequence of these processes is an almost complete absence of oxide phases of Mn in the sediments over wide areas of the Atlantis II Deep.

Nevertheless, the sedimentary stratum contains horizons sharply enriched in manganese (up to 45%). These horizons are present locally and occupy strictly defined positions both in the section and over the area of the deep. In the section of the oxide stratum, they coincide with deposits of the central oxide zone (CO) located between two sulfide zones (SU₁ and SU₂) [14]; over the area, they coincide with hypsometrically elevated areas of the sea bottom.

In the sedimentary stratum, the very existence of manganese-ore interlayers limited by sharp lithological contacts with enclosing muds indicates a change in the physicochemical conditions in the above-bottom water proceeding against the background of a calm hydrological environment excluding intensive mixing of the water masses.

The most probable cause of the change in conditions in the above-bottom water was the lowering of the level of the brines; this was connected in turn with a weakening or temporary cessation of hydrothermal activity during the formation of the manganese-ore horizons. A whole series of lithological-geochemical peculiarities of the deposits in the CO zone are evidence in favor of this assumption (the substantial admixture of biogenic-terrigenous components with the ore material, the low content of sulfides and the specifics of their isotopic composition, etc.) and also the coincidence of the manganese-ore horizons with the relatively elevated areas of the sea bottom, which find themselves in the region of layer B when the level of the brines is lowered (see Fig. 1). It is precisely in this region that conditions are created encouraging the possibility of bulk precipitation and preservation of the hydroxide compounds of manganese in the sediments due to the increase in oxygen content, the sharp fall in Fe(II) concentration, and the lowering of temperature and increase in pH value.

In Part I [6], we showed that three varieties of manganese formations, differing chiefly with respect to morphology and mineral composition, can be distinguished in the composition of the ore material: I) a primary finely dispersed mass composed of a predominantly x-ray amorphous phase in association with todorokite and a small admixture of goethite-groutite; II) reniform microconcretions of monomineralic, well crystallized manganese; III) diversely shaped concretions of intermediate (between types one and two) compositions.

Prior to discussing the possible paths and mechanisms of formation of the identified and characterized mineral varieties of manganese oxide compounds, it is advisable to briefly characterize the most general features of the processes of oxidation of Mn(II) and several of the properties of the compounds formed.

The elementary event of Mn²⁺ oxidation by oxygen in solution by virtue of the high electron capacity of the O₂ molecule during the oxidation process unavoidably leads to the formation of Mn(IV) in the form of the hydrated dioxide according to the reaction: $\text{Mn}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{OH}^- = \text{MnO}_2 \cdot \text{H}_2\text{O}$.

At the molecular level, the first hydrolyzed products of Mn²⁺ oxidation are coordinated, hydrated polymeric aggregates. Their coagulation results in the formation of encircled microstructures possessing sorption activity and capable of dehydration and intraphase redox conversion according to the scheme: $\text{Mn}^{2+} + \text{Mn}^{4+} = 2\text{Mn}^{3+}$. The course and direction of one or another conversion of the amorphous phase and the formation of individual compounds is determined principally by the conditions of interaction of Mn²⁺ with dissolved oxygen, primarily by the ratio of the concentrations of Mn²⁺ with dissolved oxygen, primarily by the ratio of the concentrations of Mn²⁺ and O₂, the pH, and also the sorption and catalytic activity of the surface of the freshly formed hydrated manganese dioxide.

Under the conditions of the Atlantis II Deep, the stratigraphy of the water stratum facilitates the differentiation physicochemical conditions associated with the environment of mineral formation.

In the diagram (see Fig. 1), we identify two zones of Mn²⁺ oxidation differing substantially with respect to an entire series of parameters.

Zone I, of active oxidation, generally coincides with brine layer C transitional to sea water and is characterized by a surplus of dissolved oxygen, a slightly alkaline environment (pH > 7) and a relatively low (<50°C) temperature. The lower-lying Zone II is distinguished primarily by an oxygen deficit and lowered pH values.

Bulk oxidation of divalent manganese occurs in the zones of active oxidation, I, where, according to the indicated scheme, the hydrated dioxide (MnO₂·H₂O) is formed. The slightly alkaline (or nearly neutral) environment facilitates a dissociation of amphoteric oxide MnO₂·nH₂O of the acidic type: $\text{MnO}_2 \cdot n\text{H}_2\text{O} \rightarrow \text{H}_2\text{MnO}_3 \rightarrow \text{MnO}_3^{2-} + 2\text{H}^+$. The MnO₃²⁻ anions formed during this process are capable of abundantly hydrated and sorbing various cations. Because of their high degree of hydration, freshly formed thixotropic macrostructures of hydrated manganese dioxide nMnO₂·mH₂O possess an especially developed surface pervious to dissolved components and possess significant sedimentational stability. Under conditions involving a highly saline background, amorphous hydroxide functions as a cation-exchanger irreversibly binding dissolved and partially hydrolyzed cations of various metals, including Mn²⁺; this accompanies its oxidation during a surplus of oxygen and results in an additional increase in the masses of individual

particles. The increase in mass (of particles primarily, due to their coagulation in combination with the oxidation mechanism) and the dehydration proceeding in parallel lead to a loss of sedimentational stability of the particles and their sinking into the lower zone II, characterized, as mentioned, by an oxygen deficit and by relatively low pH values (see Fig. 1).

Under these conditions, the possibilities of the particles for sorbing cations of metals is sharply restricted as a result of the lowering of the sorption activity in general (more acidic conditions of the environment) and the competitive absorption of Mn^{2+} cations. The oxygen deficit limits the oxidation of sorbed Mn^{2+} , and, consequently, the creation of new sorption centers. As a result, change in the composition of the particles ceases and dehydration and condensation become the primary processes of their transformation, creating conditions for subsequent crystallization and precipitation into the sediment.

Both the crystallization of the amorphous phase and its result, i.e., the formation of a specific type of structure and the degree of its ordering, are to a significant degree due to the presence large hydrated cations in sorptionally saturated complexes (aside from the temperature and pH). Because of steric limitations, the presence of sorbed cations inhibits the processes of crystallization of the amorphous phase, blocks the formation of structures with dense packing of atoms, and facilitates the formation of minerals with relatively loose anionic skeletons.

Thus, the low degree of structural order in the groundmass of the manganese-ore material and the widespread presence of weakly crystallized todorokite possessing a loose tunnel structure within the material are natural consequences of the processes of conversion of amorphous hydroxides formed in the zone of active oxidation I as described above (see Fig. 1).

The ability of thixotropic macrostructures of hydrated manganese dioxide to sorb various cations has an effect in particular on the chemical composition of the bulk, finely dispersed mass by determining the irregular distribution of the admixture of Ca, Mg, Zn, and Pb within it.

The presence of three modifications of todorokite with parameters a equalling 9.75, 19.5, and 24.4 Å within the mineral horizons apparently reflects the various degrees of saturation of the amorphous phase by metallic cations, in particular by the cations Mn^{2+} and Mn^{4+} . The degree of saturation is controlled both by concentrational and kinetic factors. In [21], it is shown that the quantity $\text{Mn}^{3+}/\text{Mn}^{4+}$ correlates directly with the dimensions of the tunnels in the structure of todorokite.

The manganese-ferruginous phase identifiable as goethite-groutite, present in small quantities in the groundmass of the ore material in association with todorokite apparently is the final product of the transformation of locally created mixed thixotropic macrostructures of amorphous iron hydrates and manganese. The formation of particles of such nature probably occurs under conditions of extremely low Fe(II) content as a result of its oxidation by hydrated manganese dioxide.

The creation of an iron-manganese phase is possible both in the upper zone of active oxidation I with the participation of Fe(II) passing into solution during microbiological oxidizing-reducing reworking of the ferruginous suspension, and in the boundary region from the upper brine to the lower due to the presence of trace quantities of hydrothermal Fe(II) there. It is apparently impossible to exclude the limited process of the spontaneous interaction $\text{Mn}^{2+} + \text{Mn}^{4+} = 2\text{Mn}^{3+}$ taking place in microregions and induced by fragmentary crystallization of goethite.

The presence of manganese-ore material in isolated reniform concretions consisting of well crystallized monomineralic manganite practically devoid of extraneous admixtures is of appreciable interest from a genetic point of view. The presence of this mineral phase in the sediments indicates that specific conditions exist in the aqueous layer for oxidation of Mn^{2+} facilitating the formation of amorphous hydroxides not containing any other cations aside from Mn^{2+} . Zone II, underlying the zone of oxidation I (see Fig. 1), completely corresponds to these conditions. Zone II is characterized by low (~ 6) pH values and elevated ($\sim 50^\circ\text{C}$) temperature.

It was noted above that oxidation of the Mn^{2+} ion by the O_2 molecule leads to the formation of hydrated manganese dioxide $\text{MnO}_2 \cdot n\text{H}_2\text{O}$. In the structure of manganite, cations of manganese exist in the trivalent state. One of the possible pathways, cations of manganese exist in the trivalent state. One of the possible pathways for the formation of Mn^{3+} consists in the interaction of $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ with Mn^{2+} cations resulting in an intraphase oxidizing-reducing process taking place. Such an interaction could be realized as a result of the lowering of the sorption activity of the surface of the particles of the hydrated dioxide under conditions of Mn^{2+} surplus. This would lead to a rapid transformation of the sorbed form to the chemical compound (salt) $\text{Mn}^{2+}\text{Mn}^{4+}\text{O}_3$ and its subsequent redox conversion $\text{Mn}^{2+} + \text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$. Despite the absence of precise experimental data, it can be assumed that the occurrence of a similar process is restricted to a specific interval of pH, since under slightly alkaline conditions a high degree of hydration both of the Mn^{2+} ion and the sorbed centers of Mn dioxide facilitate the stabilization of the sorbed form Mn^{2+} in the phase $\text{MnO}_2 \cdot n\text{H}_2\text{O}$; in acidic environments, a disproportioning of trivalent manganese takes place. Optimal pH conditions are apparently satisfied by oxidation zone II, where the hydrated manganese dioxide formed by almost instantaneously realizes its sorption capacity due to Mn^{2+} cations, which, in this case, cannot bind beyond the ratio

$\text{Mn}^{2+}:\text{Mn}^{4+} = 1:1$ in accordance with the stoichiometric reaction $\text{MnO}_2 \cdot \text{H}_2\text{O} = \text{H}_2\text{MnO}_3 + \text{Mn}^{2+} \rightarrow \text{Mn}^{2+}\text{Mn}^{4+}\text{O}_3$ and, further, $\text{Mn}^{2+}\text{Mn}^{4+}\text{O}_3 + \text{H}^+ + \text{OH}^- \rightarrow 2\text{Mn}^{3+}\text{O}(\text{OH})$.

In contrast to the strongly encircled complexes $\text{Me}^{2+}[\text{MnO}_3^{2-}(\text{nMnO}_2 \cdot \text{mH}_2\text{O})]$ formed in the zone of active oxidation I, amorphous hydroxides formed in the underlying zone II are significantly less hydrated and contain practically no sorbed cations; this facilitates their transformation to the energetically advantageous compact packing natural to manganite. Further dehydration of this phase also takes place with an increased velocity and sedimenting particles of gel encompass the entire volume; this defines the specifically spherical form of the end separations of manganite and the high degree of its crystallization. The results of a microprobe analysis confirm the almost complete absence of any other chemical elements aside from manganese in the composition of the renniform manganite nodules.

Joint sedimentation of dehydrating gel particles of todorokite and manganese composition (with a subordinate quantity of the latter) should be accompanied by the formation of mechanically mixed formations with a final habit apparently still being created in the stratum of sediments. One can assume that the most probable process is the binding of the dissolved Mn^{2+} of muddy waters with sortionally unsaturated areas of manganese dioxide. In this case, reaching the ratio $\text{Mn}^{2+}:\text{Mn}^{4+} = 1:1$ allows the formation of fragments of the structure of manganite along with the crystallization of todorokite. Other processes connected with the regrouping of the structural blocks of manganese dioxide by intraphase oxidizing—reducing interactions are possible.

The differences in rates of condensation noted above for different phases leads to the creation of mechanical interphase stresses and, as a consequence, the formation of morphologically complex, fantastical, often branching, irregular concretions.

In the case when hydrated dioxide precipitates into spherical segregations of "pre-manganite," condensed rindlike formations can be formed during the course of dehydration; the destruction of such formations can also take place as a consequence of differences in the rates of condensation and creation of metaphase stresses.

Thus, the observed mineral composition of ore material accumulated in horizons of the Atlantis II Deep are enriched with manganese as a result of diverse processes involving an ascending diffusional flux of Mn^{2+} ions from thermal solutions interacting with a flux of oxygen and particles of freshly formed amorphous hydrated manganese dioxide precipitated from above.

In general, the absence of a significant accumulation of manganese in the zone of its active oxidation indicates a balancing of the processes of formation and precipitation of particles of manganese hydroxides.

The Tethys Deep

The region of the Tethys Deep is one of the few regions of the Red Sea Rift where comparatively high hydro-thermal activity is combined with an absence of highly mineralized bottom waters (brines).

At the present time, the metalliferous sediments adjoin waters with temperatures of only 0.8°C , while the salinity is 0.4‰ higher than the corresponding parameters for regular sea water. The slight elevation of the salinity of the muddy waters in individual areas of the sedimentary stratum allows one to assume a periodic though quite insignificant variation in the mineralization of the bottom waters in the past.

When describing in Part I [6] the section studied at Site 224 and the oxide minerals of iron and manganese occurring there, we noted a clearly expressed rhythmicity in the structure of the section.

Two basic types of deposits regularly alternating in the section can be identified within the sedimentary stratum. One of these (packets II and IV) [6], is represented predominantly by iron-ore material practically devoid of biogenic-terrigenous admixture. The mineral forms of manganese are completely absent, and the content of the element does not exceed the background. The most characteristic minerals of the ore material are magnetite and lepidocrocite; goethite and hematite are present in subordinate quantities. It is important that within the iron-ore horizons magnetite is concentrated in interlayers enriched in sulfur and copper [6]; i.e., magnetite is associated with sulfides marking the stages of maximum activation of the ore process.

A second variety of sediments in the deep (packets I, III, and V) are characterized by a high content of ore material. The ferruginous component is primarily represented by lepidocrocite with an unevenly distributed admixture of hematite and goethite. It should be noted that pure goethite is encountered extremely rarely in sediments of this type, but a mixed iron-manganese phase analogous to that described in the Atlantis II Deep and identified as goethite-groutite widely occurs.

The strictly manganese component is predominantly represented by asbolans in which the degree of structural ordering increases regularly from top to bottom along the section. The weakly crystallized asbolans in packet I are the natural mineral form of manganese; they exist in association with a quantitative predominance of goethite-groutite in packets II and V [6]. An asbolanlike manganese x-phase was first observed in the topmost (20–35 cm) of the horizons investigated; it apparently is one of the initial products of the conversion of the amorphous phase to asbolan.

The limited data on the physicochemical parameters associated with the conditions of sediment accumulation in Tethys Deep and the insufficient detail in investigations of deposits present in the deep only allow us to represent the regime and dynamics of the ore-forming process and to discuss the basic mechanisms of formation for the oxide phases of iron and manganese in a preliminary form, a form more generalized than that for the Atlantis II Deep.

The clearly expressed rhythmical structure of the section of hydrothermal deposits accompanied by sharply differing chemicomineralogical characteristics most probably reflects a periodic alteration in intensity and a pulsational character for the operation of the hydrothermal source.

Iron-ore horizons II and IV correspond to the activation stages in the ore-forming process. These periods are characterized by an inflow of large quantities of Fe(II) and Mn(II) to the bottom waters; the mixture of these cations with oxygen-containing sea water in the thermal solutions is accompanied by oxidation of the reduced forms, mainly of iron.

A series of laboratory investigations have now established that the oxidation of Fe(II) in neutral or slightly alkaline solutions leads to the formation of lepidocrocite or magnetite. The suggestion has been made that the conversion of an amorphous substance to one or another mineral phase is controlled primarily by kinetic factors. Rapid oxidation facilitates crystallization of lepidocrocite; slow oxidation facilitates the crystallization of magnetite [20]. Apparently, it is primarily the ratio of the concentrations Fe(II) and O_2 , i.e., the conditions of oxidation of divalent iron, which affect the kinetics of the process.

It was mentioned above that interlayers of sediments sharply enriched in magnetite correspond to periods of high hydrothermal activity in the Tethys Deep. It can be assumed that it is precisely during these periods that the ratio of Fe(II) and O_2 concentrations in sea water ($Fe(II) \gg O_2$) allow for the coprecipitation of amorphous hydroxide and hydroxo-acidic forms of iron with the formation of magnetite occurring during the dehydration and crystallization of these forms. The possibility of forming magnetite as a result of the crystallization of a gel containing both Fe(II) and Fe(III) has been confirmed experimentally [15].

A certain lowering of the hydrothermal activity is accompanied by a decrease in the content of Fe(II) in the solution; this, under conditions of the surplus of oxygen leads to a high rate of oxidation of iron and the formation of lepidocrocite. Small quantities of goethite and hematite in iron-ore sediments are most probably products of the transformation of lepidocrocite.

Under conditions involving high concentrations of Fe(II), active consumption of oxygen leads to a rapid exhaustion of its supply and a temporary filling of the deep with oxygen-free waters enriched in Mn(II) and containing the nondeoxygenated fraction of Fe(II). Under similar conditions, a complete absence of iron-oxide compounds in the ore material of packets II and IV would be completely logical, since all of the oxygen from the water filling the deep would be consumed in the oxidation of the iron, a portion of which would remain in the solution in the form of Fe(II).

In periods of weakened intensity of hydrothermal activity, the parameters of the water mass filling the deep gradually balance with the parameters of the sea water as a result of diffusional and convective movement and conditions are thus created for the oxidation of both the remaining Fe(II) in solution and the Mn(II) which accumulates there; conditions are also created for the oxidation of small portions of Fe(II) and Mn(II) arriving to the bottom waters as a result of the fading of the ongoing hydrothermal process.

These periods correspond to sediment packets (I, III, and V) [6] sharply enriched in biogenic—terrigenous material and characterized by a mixed iron—manganese composition of ore material.

The joint sedimentation of hydroxides forms of iron and manganese in approximately equal quantitative ratios ($Fe:Mn = 0.8:1.09$) indicates relatively low concentrations of Fe(II) insufficient for significant reduction (under slightly alkaline conditions) of the hydrated manganese dioxide formed in the upper, more aerated layers of the water stratum.

The oxidation of divalent iron led, as was mentioned earlier, to the formation of lepidocrocite, which is partially transformed in the sediment to goethite and hematite. This transition was probably inhibited to a significant degree by the presence of amorphous silica and hydrated Mn dioxide; it also required time, a fact confirmed by the extremely low concentrations of goethite in the upper portion of the section, where lepidocrocite is practically the only mineral phase of oxidized iron [6].

The primary features associated with the formation of the complex of manganese minerals found in the Tethys Deep could be presented by building upon the theoretical assumptions mentioned above concerning the behavior of Mn and its hydroxide forms under competitive physicochemical conditions. We should note first of all that, in contrast to the zone of oxidation I in the Atlantis II Deep, the aqueous stratum in the Tethys Deep is characterized by more alkaline

conditions, by an oxygen deficit created as a result of previous oxidation of Fe(II), and by substantially smaller concentrations of Mn(II). It is apparent that these conditions impeded a rapid accumulation of a mass of suspended manganese dioxide particles as a result of their coagulation. Apparently, aggregates which were two-dimensional, octahedral networks of octahedrons joined by edges were formed during the first stage in this case; Mn^{4+} cations were located in the centers of the aggregates, with the O atom and the OH group serving as anions. Such polymeric aggregates realized their sorptional possibilities predominantly as a result of Mn^{2+} . Thus, it is possible that, due to slow coagulation, weakly ordered hydrated structures initially arose with adsorbed Mn^{4+} cations and H_2O molecules adjoining fragments of islandlike octahedral Mn^{4+} layers above and below. Intraphase oxidizing—reducing reactions between Mn^{4+} and adsorbed Mn^{2+} were inhibited because of the high degree of hydration of the polymeric microaggregates under consideration. It is apparent that the condensation, agglutination, and also the mutual orientation of these microaggregates led to a layered alternation of two-dimensional associations of Mn^{4+} and Mn^{2+} . During the course of the dehydration and thickening, structural reorganizations of the Mn^{2+} cations and the H_2O molecules were possible, resulting in the creation of two-dimensional nuclei consisting of Mn^{2+} associations in an octahedral environment of H_2O and OH molecules. In parallel with the formation of an ever more crystallized structure, an intraphase oxidizing—reducing interaction of Mn^{4+} and Mn^{2+} apparently took place, resulting in the appearance of trivalent manganese. Probably, this stage corresponded to the weakly ordered phase containing layers (or islands of layers) populated with Mn^{4+} , Mn^{3+} , and Mn^{2+} cations. This phase can logically be considered as preasbolan, since, when the content of Mn^{2+} relative to Mn^{4+} is comparatively low, all of the sorbed Mn^{2+} would be used up during the course of the oxidizing—reducing interaction between them, with only two valent forms of manganese, Mn^{4+} and Mn^{3+} remaining in the structure, which is characteristic of the asbolans which have been described. Thus, the alternation of layers of tri- and quadrivalent forms of manganese predetermined the initial ordered alternation of sorbed polymeric complexes. The disruption of the local balance of valences during the course of a reaction of the type $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+} + 2\text{Mn}^{3+}$ could be compensated for by a redistribution of the electron density within the structure of the mineral, which would be accompanied by a localization of Mn^{4+} in layers of one type and Mn^{3+} in layers of a different type. This difference would be determined by features associated with the electron shells of the differently valent cations of manganese; it would lead mainly to an oxy octahedral grouping for Mn^{4+} and a hydroxyl grouping for Mn^{3+} and Mn^{2+} . It should be noted that the appearance of hydroxide layers containing Mn^{3+} could be connected not only with the oxidizing—reducing interaction of Mn^{4+} and Mn^{2+} , but also with a partial oxidation of Mn^{2+} cations in the interlayer structures by the free oxygen of the sea water.

The formation of the groundmass of goethite-groutite in the Tethys Deep can be well explained from the point of view of the processes described above.

Thus, the high degree of hydration of $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ under the conditions of an alkaline environment allowed a substantial sorptional absorption of partially hydrolyzed Fe(II). The burial of such a sorbed complex in the sediment and its dehydration and crystallization over the course of geological time opened the way for the intraphase oxidizing—reducing interaction: $\text{Fe(II)} + \text{Mn(IV)} \rightarrow \text{Fe(III)} + \text{Mn(III)}$. The final product of these types of conversions apparently was the mixed ferruginous-manganese phase of goethite-groutite. The predominance of goethite-groutite in the lower horizons of sediments enriched with manganese (packets III and V) [6] and its almost complete absence in the upper packet I is an indication of the relative duration of the process involved in the formation of the mineral.

The suggested mechanism of formation of goethite-groutite is the simplest and most probable, however it needs experimental verification.

In general, the more uniform composition and the morphological peculiarities of the hydroxide forms of Mn in the Tethys Deep compared to the Atlantis II Deep and also the ubiquitous (rather than local) deposition of these forms over the area were mainly due to the absence of differentiation in the conditions of precipitation of amorphous hydrated Mn dioxide from solution. This, in turn, was connected primarily with the morphometry of the deep and with the character of the ore forming process.

Thus, the association of manganese minerals present in the ore material of hydrothermal-sedimentary accumulations with the Atlantis II Deep and Tethys Deep (the Red Sea) was formed as a result of the oxidation of the Mn(II) present in the composition of the thermal springs and the precipitation of the amorphous hydrated manganese dioxide from the solution.

Further pathways of conversion of the gellike amorphous material and individual crystal phases depend upon the composition and were controlled by a complex combination of oxidizing—reducing, coordinational, colloidal-chemical, and sorptional, sedimentational, and diagenetic effects and also by the kinetic parameters of the dehydration of the gel formations. All of the effects enumerated were controlled, as was shown above, by the concrete physico-chemical conditions of the mineral-forming environment.

It should be kept in mind that many of the positions and details of the proposed mechanisms are, to a significant degree, hypotheses and require further, deeper investigation with an arrangement of special experiments under conditions resembling those in nature.

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VARIATION OF PHYSICAL PROPERTIES OF MATERIAL COMPOSITION OF
SEDIMENTS IN THE NORTHWESTERN SEA OF JAPAN DURING THE LATE
PLEISTOCENE AND THE HOLOCENE

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In a study of the sediments from the northwestern Sea of Japan, physical properties (moisture content, volumetric weight, magnetic susceptibility, natural remanent magnetization, and the type of magnetization of ferromagnetic fraction), the chemical composition, and (selectively) mineral composition of this type of sediment are described. A stratigraphic classification of sediments is constructed according to the concentration of diatom algae. The results are used to examine the influence of paleogeographic settings and diagenetic processes on alteration of the physical properties of sediments in the region and their material composition during the Holocene and the Late Pleistocene.

Concentrations of authigenic minerals, sediments, and interstitial waters are known to change in seafloor sediments of marginal basins as a result of changes in sedimentation settings and varied intensity of diagenetic processes associated with oxidation of organic matter [1]. This involves variation of such physical properties as magnetic susceptibility, natural remanent magnetization, moisture content, and volumetric weight of the sediments [7]. The type and intensity of diagenetic processes are determined by the geochemical conditions of natural water, the top layer of sediments, and the amount of organic matter in them. Extreme examples of diagenetic processes are oxidative conditions of pelagic red clays and reductive conditions of sediments in the Black Sea and other stagnant basins.

Sedimentation settings and concentration of sediments in the aquatoria of near-continental areas are largely controlled by the climate, sea level fluctuations, and similar factors [9, 17]. For marginal basins, however, it is sometimes unclear whether the change in physical properties and the composition of sediments has been caused by diagenesis or an alteration of the paleogeographic environment and sedimentation conditions — and to what extent the two aspects are interrelated.

The authors have investigated sediments from three columns in the northwestern Sea of Japan (Fig. 1). Two cores (K-13-4 and K-13-5) were collected from the middle portions of the continental slope in the Primorye area (44°09.2' N lat., 137°01.1' E long., and 45°56.0' N lat., 138°35.4' E long.; the depths are 1470 and 1500 m, respectively). The third column (K-13-2) was taken at the base of the continental slope (43°46.8' N lat., 136°54.5' E long.; depth 3300 m) in the northern extremity of the central deep-sea basin. The lithologic composition of the sediments, based on a visual description and an investigation of polished sections (done by V. V. Eremeeva and N. G. Brodskaya, Geological Institute, USSR Academy of Sciences), is given in Fig. 2.

The pelitic sediments of the top portions of the column give way, down the section, to coarser-grained sediments with siltstone interlayers and gravel and pebble inclusions, presumably associated with glacial transport (see Fig. 2). The homogeneous structure of sediments is replaced by a stratified structure in the same sequence. The core K-13-5, unlike the other columns, exhibits larger granulometric units and a better structural homogeneity. A slight hydrogen sulfide odor and dark gray color with a green or blue tinge indicate reducing conditions inside the sedimentary strata. The examination of polished sections provides a notion of the mineral composition. The terrigenous minerals include quartz, plagioclases, pyroxene, epidote, zircon, and sphene; diagenetic minerals include iron hydroxides, pyrite, calcite, and glauconite. The biogenic component is represented by diatoms, single foraminifers, and clots of organic matter. Volcanic glass is frequent.

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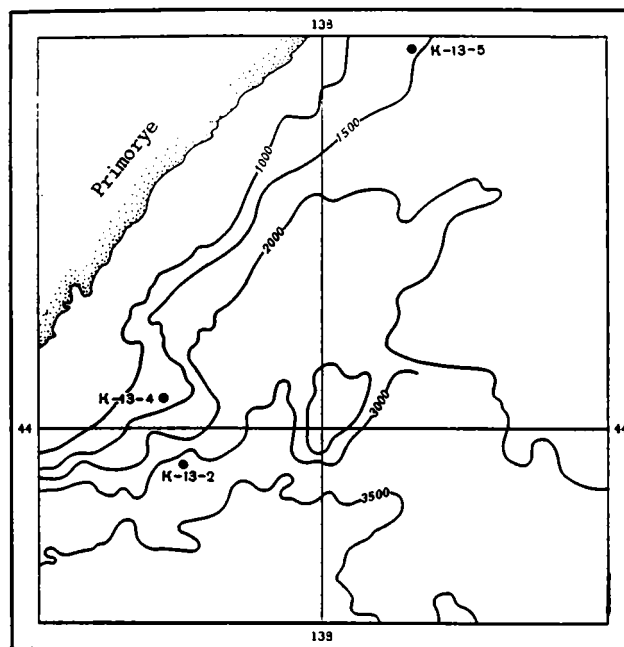


Fig. 1. Location of sampling sites.

The moisture content W and the volumetric weight Δ of sediments were measured on board ship by the standard methodology, using Litvinov's field lab unit.

Magnetic susceptibility κ and natural remanent magnetization J_n of sediments were measured on board ship using an IMV-2 kappameter and an ION-1 remanent magnetization measurement unit. Specimens were taken with a spacing of 5-10 cm along the entire core. Onboard investigations also included a temperature-time cleaning of specimens in permalloy containers and repeated measurement of the direction and magnitude of the stable of the component of the J_n vector. Specimen cleaning was done at 70-80°C. The duration of cleaning was determined according to the following standard technique. Control specimens, taken with a spacing of 50 cm along the core, were heated at a given temperature during 1 hr and cooled to room temperature. The magnitude and direction of the remanent J_n were then measured. The time of specimen heating was then increased successively by 1 h and the measurements were repeated; the total time of thermal treatment was 20 h. Cleaning time was determined as the total heating time until the point when the angular parameters of the vector J_n no longer changed; it was 4-8 h. All specimens were heated for 10 h to ensure reliability of results.

Normal magnetization curves [15] and thermomagnetic curve were plotted for specimens to determine the composition of the ferromagnetic fraction of sediments. Unlike the common methodology [15], the specimens were magnetized to saturation prior to each heating to obtain thermomagnetic curves. The temperature was raised (from room temperature) consecutively by 50°C.

The portion of saturation magnetization J_n (T °C) that remained after heating at a temperature T °C was measured at room temperature. With this method it was possible to isolate distinctly the temperature interval in which a new ferromagnetic was formed. Laboratory investigations were conducted on Avchyan's equipment [15]. The composition of clay minerals and the quartz-to-plagioclase ratio in the sediment were determined on a DRON-3 x-ray diffractometer using the standard method (analyst I. V. Kholodkevich, Far Eastern Geological Institute, Far East Scientific Center, USSR Academy of Sciences). The chemical composition of sediments was determined by the silicate analysis method [14] (analysts A. V. Renkas, G. A. Skrinnik, and M. A. Shaikevich, Institute of Geophysics and Mineralogy, Ukrainian Academy of Sciences). Amorphous silica content was determined by L. Yu. Odinkova (Far Eastern University) by alkaline extraction.

Stratigraphic division of sediments in the cores was based on boundaries of a sudden change of the ecologic composition of the diatom algae set, a change in the abundance α of valves per gram of dry sediment, and variations in the number of individuals of warm-water species to the total number of individuals in a complex T_d [21]. The parameters α and T_d correlate strongly with the presence of modern diatoms of the zonal species *Denticulopsis seminae* at the very bottom of the cores, indicating that the age of the sediments is not older than the Late Pleistocene, because this form appears in pelagic sediments of the Pacific Ocean at the boundary between the Middle and Late Pleistocene [11,

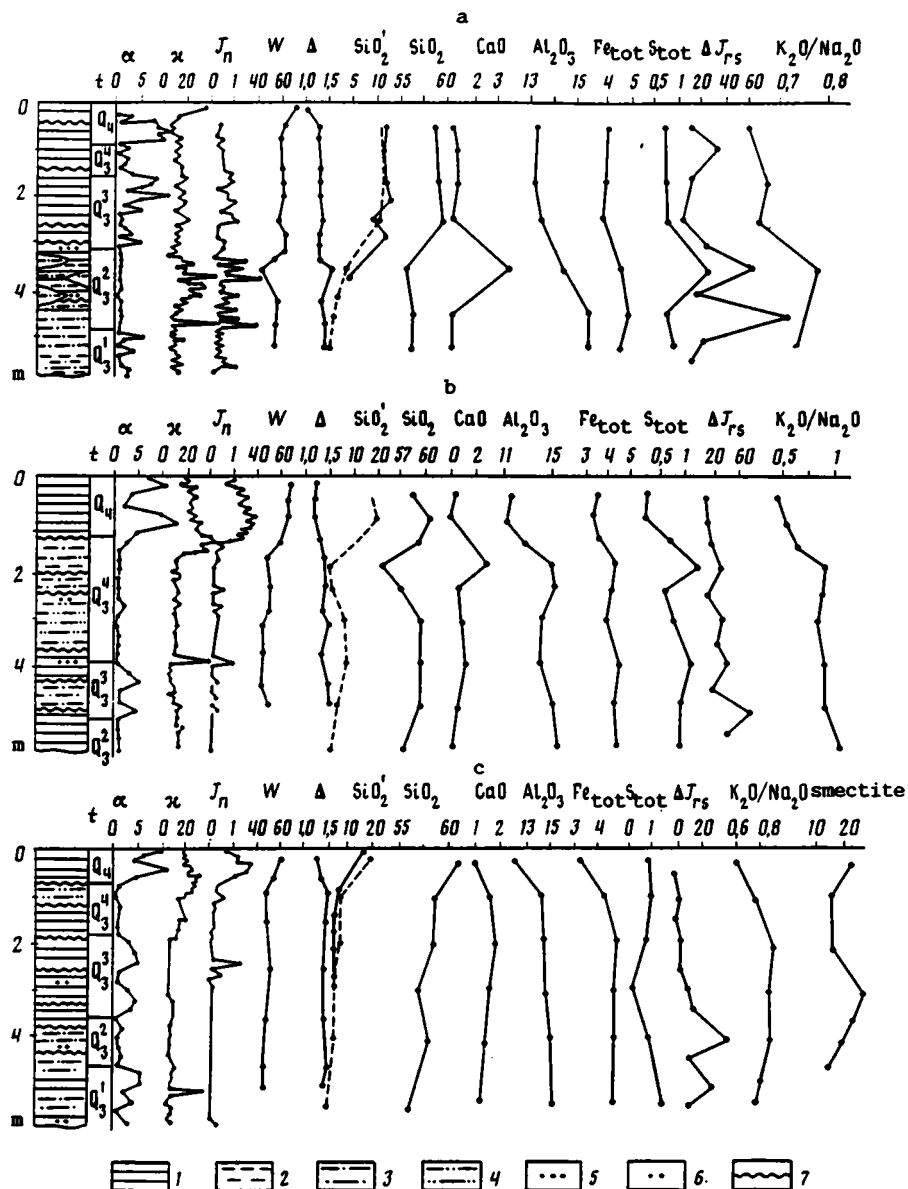


Fig. 2. Lithologic composition of sediments in columns K-13-2 (a), K-13-4 (b), and K-13-5 (c) and variations of their physical and chemical characteristics in sections: 1) pelitic ooze; 2) silt-pelitic ooze; 3) fine silt; 4) coarse silt; 5) small gravel; 6) small pebble; 7) sharp lithologic contact; t is sediment stratigraphy according to diatoms; α is the number of diatoms (million individuals per 1 g of dry sediment); κ (12.5×10^{-6}) is magnetic susceptibility; J_n ($10^{-3} \text{ A} \cdot \text{m}^{-1}$) is natural remanent magnetization; W (%) is moisture content; Δ ($\text{g} \cdot \text{cm}^{-3}$) is volumetric weight; ΔJ_{rs} (%) is the relative increment of remanent saturation magnetization after heating to 650°C ; κ_T is magnetic susceptibility after heating specimen to 650°C (% relative to κ); smectite (%) is the proportion of smectite in clay minerals; chemical composition (5); SiO_2' is amorphous silica concentration (solid: analytic; dashed: calculated [8]).

18, 25]. Qualitative and quantitative investigations of the species composition of diatoms in the section of the cores according to the method described in [10] identified seven sets, making it possible to compare them in time terms (see Fig. 2).

Set 1 is characterized by a high abundance of diatoms (up to 5 million valves per gram of sediment) and warm-water structures (T_d to 50%). The characteristic diatom set consists of moderately warm- and warm-water species: *Coscinodiscus wailessii* (to 4%), *C. radiatus* (to 15%), *C. perforatus* (to 8.5%), *C. nodulifer* (to 4.8%), *Thalassiosira*

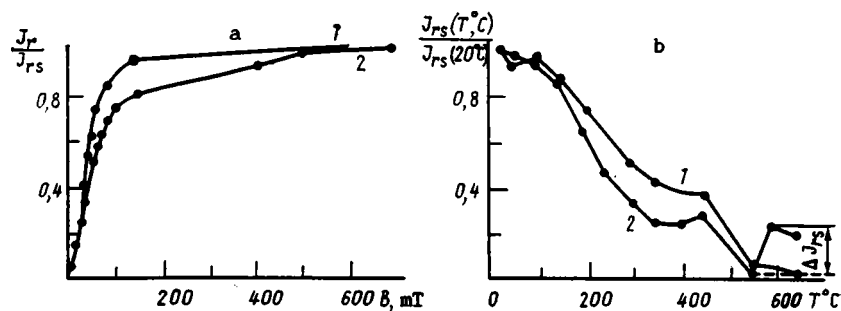


Fig. 3. Typical normal magnetization curves (a) and thermodemagnetization curves (b) of sediments from column K-13-4 sampled at 50 (1) and 350 cm (2) from the top. $J_r(T, ^\circ C)$ = remanent saturation magnetization after heating to $T^\circ C$; $J_{rs}(20^\circ C)$ = remanent saturation magnetization at room temperature; B = magnetic field inductance, mT.

lineata (to 9%), *Th. oestrupii* (to 7%), *Planktonilla sol* (to 8.4%), and *Thalassionema nitzschioides* (11.2%). Among cold-water species *Thalassiosira excentrica* (to 20%) and *Coscinodiscus marginatus* (to 10%) were predominant. A comparison of the species composition of the diatoms and their ecologic structures with Late Pleistocene sets of the Northwestern Pacific [3] suggested that this set belongs to Riss-Würm Interglacial Q^1_3 (isotopic stage 5e). The presence of *Rhizosolenia curvirostris* supports this dating [11].

Set 2 is characterized by a low abundance of diatoms and a low content of warm-water species ($T_d = 1-10\%$). The core of this set consists of cold-water *Thalassiosira gravida* (to 17.5%), *Th. nordenskiöldii* (to 8%), and *Th. excentrica* (to 35.4%). This set was formed in the early Würmian Q^1_3 (isotopic stage 5d), when a cooling of the climate shifted cold-water diatom habitats southward [3-11].

Sets 3-5 have a moderate ecologic structure (T_d to 30%) and an abundance of up to 5 million valves per gram of sediment and more. Typical heat-loving species are: *Coscinodiscus radiatus* (to 10%), *C. perforatus* (to 8.1%), *Actinocyclus curvatulus* (to 18%), and *A. diviatus* (to 11.7%). The main form of the set is *Rhabdonema arcuatum* var. *ventricosa*. Of the cold-water species, the main ones are *Coscinodiscus marginatus* (to 9%), *C. oculus-iridis* (to 18%), and *Thalassiosira excentrica* (to 12%). Complex 4 is characterized by an increase in the abundance of cold-water species (to 80%) and corresponds to the glaciation of isotopic stage 4. Complexes 3 and 5 represent a warming of the Middle Würmian Q^3_3 (isotopic stages 5a-5c and 3). The dating of sets 3-5 is based on their correlation with the diatoms of horizon III in sediments of the Northwestern Pacific, isolated by Zhuze [3].

Set 6 is characterized by a low abundance of valves and a virtually complete absence of warm-water flora ($T_d = 1-3\%$). The core of the set consists of arctoboreal and northern-boreal species *Thalassiosira gravida* (to 18%), *Th. excentrica* (to 35%), *Th. nordenskiöldii* (to 11%), *Chaetoceros* spores (to 28%), and others. Redeposited Tertiary and freshwater species are found, indicating a transport from older sediments. The set corresponds to the most advanced glaciation stage of the Late Würmian Q^3_4 (isotopic stage 2). A nearly complete absence of warm-water species is the characteristic trait of the diatom set of that time.

Set 7 numbers up to 10 million valves per gram of sediment (T_d to 30-35%); it was formed by the Recent flora of the northwestern Sea of Japan [10]. It corresponds to the Holocene Q_4 .

Normal magnetization and thermal demagnetization curves have been constructed for the ferromagnetic fraction of the sediments. The specimens for this study were taken from the cores with a spacing of 50 cm (typical curves of two specimens from core K-13-4 horizons of 50 and 350 cm are shown in Fig. 3). The magnetization curves indicate that hematite and iron hydroxides play no important role in the formation of J_n , since saturation is achieved at magnetic field inductions of 100-150 mT. Curie points estimated for sedimentary material from thermomagnetic curves vary from 200 to 580 $^\circ C$. This suggests that the main ferromagnetic in these sediments is titanomagnetite. A bend on thermal demagnetization curves at temperatures from 300-400 to 550-600 $^\circ C$ is probably a reflection of iron sulfide transmutation to magnetite and then hematite. The remainder of saturation magnetization ΔJ_{rs} after transformation appears to be proportional to the concentration of the newly formed ferromagnetic. A comparison of the curves of ΔJ_{rs} and the magnetic susceptibility of sediments heated to 650 $^\circ C$ (κ_T) (see Fig. 2) supports this hypothesis, since the magnetic susceptibility is proportional to the concentration of the ferromagnetic component.

Five specimens from the top and bottom of cores K-13-4 and K-13-5 were reprecipitated with the standard method to investigate the type of magnetization [15]. The reprecipitation factor was 0.7-1.2, suggesting that sediment

TABLE 1. Contents of Principal Rock-Forming Elements in Cores, %

Horizon, cm	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Fe _{tot}	MnO	MgO	CaO	Na ₂ O	K ₂ O	S	SO ₃	S _{tot}	P ₂ O ₅	CO ₂	SiO ₂ -4Al ₂ O ₃	K ₂ O/ /Na ₂ O	K *
K-13-2																			
50	58,67	0,74	13,1	3,14	2,16	3,88	0,08	2,19	1,09	3,57	2,29	0,6	0,3	0,72	0,14	5,02	6,11	0,64	1,12
	53,63	0,83	14,67	3,52	2,42	4,35	0,09	2,45	1,22	4,0	2,56	0,67	0,34	0,81	0,16	5,62	—	—	—
165	58,68	1,04	12,95	3,1	2,16	3,85	0,16	2,14	1,09	3,38	2,29	0,76	—	0,76	0,15	5,22	6,88	0,68	1,13
	53,24	1,18	14,63	3,5	2,44	4,35	0,18	2,42	1,23	3,82	2,59	0,86	—	0,86	0,17	5,90	—	—	—
250	59,49	1,04	13,28	3,12	2,02	3,75	0,12	2,3	0,99	3,47	2,29	0,78	—	0,78	0,15	4,9	6,37	0,66	1,12
	54,25	1,16	14,87	3,49	2,26	4,2	0,13	2,58	1,11	3,89	2,56	0,87	—	0,87	0,17	5,49	—	—	—
350	55,88	0,84	14,23	4,27	1,87	4,44	0,2	2,33	3,38	2,93	2,29	1,54	0,45	1,72	0,14	6,32	-1,04	0,78	1,04
	54,32	0,87	14,79	4,44	1,94	4,61	0,21	2,42	3,52	3,05	2,38	1,65	0,47	1,79	0,15	6,57	—	—	—
445 †	56,44	1,04	15,25	4,53	2,02	4,74	0,19	2,82	1,09	3,07	2,34	0,76	—	0,76	0,15	3,57	-4,56	0,76	1
520 †	56,16	0,84	15,21	3,99	2,3	4,58	0,24	2,76	0,99	3,2	2,32	0,96	—	0,96	0,15	3,75	-4,68	0,73	1
K-13-4																			
40	58,83	0,74	11,34	3,49	1,3	3,45	0,06	2,06	1,01	4,35	1,8	0,28	—	0,28	0,12	6,2	13,47	0,41	1,22
	50,11	0,9	13,83	4,26	1,59	4,21	0,07	2,51	1,27	5,31	2,20	0,34	—	0,34	0,15	7,56	—	—	—
90	60,46	0,62	11,2	2,75	1,86	3,37	0,05	2,2	0,92	3,94	2,01	—	0,51	0,2	0,08	5,53	15,66	0,51	1,25
	50,76	0,78	14	3,44	2,33	4,21	0,06	2,75	1,15	4,93	2,51	—	0,64	0,25	0,1	6,91	—	—	—
140	59,28	0,66	12,76	2,9	2,08	3,66	0,05	1,93	1,49	3,54	2,13	0,56	0,44	0,72	0,11	6,6	8,24	0,59	1,14
	53,30	0,75	14,55	3,31	2,37	4,17	0,06	2,2	1,7	4,04	2,43	0,64	0,5	0,82	0,13	7,52	—	—	—
190 †	55,47	0,74	14,94	2,74	2,95	4,21	0,06	2,48	2,48	2,98	2,77	1,2	0,51	1,4	0,12	5,72	-4,29	0,92	1
	53,63	0,79	15,23	3,07	2,65	4,21	0,06	2,41	1,29	2,98	2,77	0,45	0,41	0,61	0,13	4,24	-3,29	0,92	1,01
240	57,2	0,8	15,38	3,1	2,68	4,25	0,06	2,43	1,3	3,01	2,8	0,45	0,41	0,62	0,13	4,28	—	—	—
	59,72	0,7	14,33	3,78	1,65	3,92	0,06	2,41	1,49	3,2	2,64	0,58	0,32	0,71	0,09	3,83	2,4	0,83	1,07
310	56,74	0,75	15,33	4,04	1,77	4,19	0,06	2,58	1,59	3,42	2,82	0,62	0,34	0,76	0,1	4,1	—	—	—
400	59,72	0,74	14,14	4,5	1,72	4,49	0,08	2,3	1,44	3,0	2,64	1,02	0,25	1,12	0,1	3,42	3,16	0,88	1,08
	56,45	0,8	15,27	4,86	1,86	4,85	0,09	2,48	1,56	3,24	2,85	1,1	0,27	1,21	0,11	3,69	—	—	—
490	59,50	0,84	15,04	4,18	1,65	4,2	0,10	2,38	1,19	2,88	2,64	0,82	0,31	0,94	0,12	3,09	-0,66	0,92	1,04
	58,1	0,87	15,64	4,35	1,72	4,37	0,1	2,48	1,24	3,0	2,75	0,85	0,32	0,98	0,12	3,2	—	—	—
580	58,10	0,79	15,39	3,58	2,37	4,34	0,08	2,54	0,99	2,69	2,96	0,89	0,25	0,99	0,09	3,26	-3,46	1,1	1,01
	57,84	0,8	15,54	3,62	2,39	4,38	0,08	2,57	1,0	2,72	2,99	0,9	0,25	1,0	0,09	3,29	—	—	—
K-13-5																			
20	61	0,57	11,87	1,13	2,95	3,08	0,04	2,33	0,99	3,52	2,12	0,8	0,43	0,97	0,05	5,64	13,52	0,6	1,22
	52,48	0,70	14,48	1,38	3,6	3,76	0,05	2,84	1,21	4,29	2,59	0,98	0,52	1,18	0,06	6,88	—	—	—
100	58,85	0,84	14,24	3,32	2,16	4,0	0,07	2,41	1,49	3,08	2,4	0,77	0,49	0,97	0,14	4,38	1,89	0,78	1,07
	56,18	0,9	15,24	3,55	2,31	4,28	0,07	2,58	1,59	3,3	2,57	0,82	0,52	1,04	0,15	4,69	—	—	—
200	58,56	0,74	14,35	2,03	4,31	4,77	0,05	2,23	1,74	2,96	2,62	0,7	0,33	0,83	0,09	4,98	1,16	0,88	1,06
	56,12	0,78	15,21	2,15	4,57	5,05	0,05	2,36	1,84	3,14	2,78	0,74	0,35	0,88	0,16	5,28	—	—	—
295	57,19	0,82	14,73	2,35	4,02	4,76	0,05	2,41	1,49	3,07	2,62	0,14	0,32	0,27	0,11	5,69	-1,73	0,86	1,03
	56,09	0,84	15,17	2,42	4,14	4,9	0,05	2,48	1,53	3,16	2,7	0,14	0,33	0,28	0,11	5,86	—	—	—
400	57,81	0,8	14,74	4,75	1,86	4,77	0,05	2,34	1,19	3,07	2,62	1	0,22	1,09	0,09	5,24	-1,15	0,86	1,03
	58,14	0,82	15,18	4,89	1,92	4,91	0,05	2,41	1,23	3,16	2,7	1,03	0,23	1,12	0,09	5,4	—	—	—
550 †	55,90	0,76	15,09	3,87	2,65	4,77	0,09	2,46	1,09	3,27	2,5	1,14	0,22	1,53	0,11	6,64	-4,46	0,77	1

Note. The first value gives the concentration in the natural sediment; the second value is as estimated for the abiogenic component. K* is the coefficient for recalculation of contents relative to abiogenic component, equal to 100/100 SiO₂ (amorph.). In the recalculations of SiO₂, the value of SiO₂ (amorph.) was subtracted from the original value; S = sulfide sulfur; SO₃ = sulfate and elemental sulfur; † = for equal contents one figure is given.

TABLE 2. Correlation Coefficients of Terrigenous Element Contents in Sedimentary Columns

Component	TiO ₂	Al ₂ O ₃	Fe _{tot}	MnO	MgO	Na ₂ O	K ₂ O
Column K-13-2							
SiO ₂	—0,25	0,99	0,75	0,58	0,94	—0,75	—0,88
TiO ₂		—0,16	—0,43	—0,14	—0,04	0,35	0,50
Al ₂ O ₃			0,67	0,56	—0,97	—0,69	—0,83
Fe _{tot}				0,68	0,54	—0,92	—0,90
MnO					0,41	—0,83	—0,77
MgO						—0,51	—0,68
Na ₂ O							0,94
Column K-13-4							
SiO ₂	—0,16	0,99	0,37	0,45	—0,15	—0,96	0,90
TiO ₂		—0,15	0,16	0,58	0,11	0,31	—0,36
Al ₂ O ₃			0,39	0,47	—0,14	—0,95	0,89
Fe _{tot}				0,70	0,02	—0,34	+0,43
MnO					0,02	0,33	0,30
MgO						0,20	0,16
Na ₂ O							—0,91
Column K-13-5							
SiO ₂	0,74	0,99	0,83	0,25	—0,90	—0,99	—0,09
TiO ₂		0,78	0,32	0,07	—0,40	—0,66	—0,24
Al ₂ O ₃			0,80	0,19	—0,87	—0,98	—0,06
Fe _{tot}				—0,01	—0,97	—0,90	—0,07
MnO					—0,09	—0,17	—0,03
MgO						0,94	—0,08
Na ₂ O							0,10

TABLE 3. Clay Mineral Compositions (%) and Quartz/Plagioclase Content Ratio in Column K-13-5

Mineral	Horizon, cm							
	5—10	25	95	210	310	360	410	455
Smectite, 17 Å	21	24	17	17	31	24	20	14
Hydromica, 17 Å	46	44	55	49	46	48	53	54
Chlorite, 7 Å	33	32	28	34	23	28	27	32
Quartz/plagioclase	—	0,76	0,56	0,67	—	—	—	—

magnetization is orientational. The magnetic and mineralogic analysis thus determined the composition of ferromagnetic fractions of the sediments, proving that they are usable for paleomagnetic studies.

A paleomagnetic investigation of cores K-13-2, K-13-4, and K-13-5 showed an inclination of the ancient geomagnetic field within the range of +45 to 65°; this means that all the sediments accumulated during a polarity of normal polarity, which matches their Upper Pleistocene age.

Variations of the physical properties and chemical composition are observed in the cores (see Fig. 2). Since the collection sites were in 5 different geomorphologic entities of the basin floor with different sedimentation conditions, the data must be examined separately for the cores according to their geomorphologic properties.

Cores K-13-4 and K-13-5, sampled from the middle of the continental low-angle slope, display a change in physical properties (magnetic susceptibility, natural remanent magnetization, moisture content, volumetric weight, and chemical composition) in the intervals of 100–170 and 20–100 cm, respectively (see Fig. 2). Transient zones of the physical characteristics of the sediments at column tops are determined more precisely due to more detailed sampling: 120–170 cm for K-13-4 and 50–100 for K-13-5. They correspond to boundary sediments of the Late Würmian glaciation Q₃⁴ and the Holocene.

We will examine the possible factors responsible for the change of the magnetic properties of sediments. A drop in magnetic susceptibility and natural magnetization with approach to the bottom of the transient zone is associated with a decrease of ferromagnetic material concentration. This is confirmed by a decrease in the quantity of the ferromagnetic fraction isolated from the specimen down the column by magnetic separation. Initially, the variations of κ and J_n in these columns were attributed to formation of magnetic sulfides of iron in the course of hydrotroilite transformation to pyrite [16]. A magnetic-mineralogic study did not confirm this hypothesis.

It was previously believed that magnetite and titanomagnetite are chemically stable minerals in a natural environment [6]. Recent studies [19, 22], however, allow for an unstable chemical condition of magnetite in marine sediments and a reduction of the volume of ferromagnetic grains after their diagenetic alteration. Some authors [23, 24, 27] assume that the drop of κ and J_n down the column reflects pyritization of the finest fraction of the ferromagnetic component. This change of κ and J_n along the core has been observed in sediments from the Sea of Japan to the north of the Yamato rise [23], the Gulf of California, and the Congo alluvial cone [27]. A decrease of κ and J_n down the column is often associated with a rise in pyrite content. Many Japanese investigators assume in their stratigraphic division of sediments from the Sea of Japan that pyrite indicates a transition from Holocene to glacial sediments [20].

According to available data [2, 23], oxygen content in bottom water in this basin during the last glacial sea regression, in contrast to the Recent level, was low. This activated sulfate-reducing bacteria, which oxidized organic matter and formed sulfides. Higher C_{org} contents in glacial sediments and at the boundary with the Holocene were conducive to these developments [2, 26]. The mineral (pyrite in glyphs) and chemical composition and the values of ΔJ_n in cores K-13-4 and K-13-5 indicate a slight rise of sulfide sulfur (mainly pyrite). Such early diagenesis of sediments may be one of the factors responsible for the decline of κ and J_n in glacial sediments Q_3^4 .

It is assumed [1, 13] that in aerobic/anaerobic environments pyrite is formed as a result of interaction of hydrogen sulfide mainly with dissolved ferrous iron and in anaerobic conditions with clastic iron. At this point, we lack data to confirm a transition of magnetic minerals of clastic iron fraction to nonmagnetic minerals in the course of diagenesis. In addition, a portion of the magnetic material is encased in a silicate shell and does not dissolve [4].

The behavior of magnetic susceptibility and natural remanent magnetization in the section of cores K-13-4 and K-13-5 can be caused also by a reduced influx of detrital ferromagnetic minerals to sediments of the middle portion of the continental slope during the glacial time as compared with the Holocene.

It has been established [9] that transport of matter from the first avalanche sedimentation level situated in river deltas and on the upper shelf to the second level — the base of the continental slope — is sharply intensified during sea regressions. Thus, in glacial times, accumulation of reworked marine sediments is increased on the continental slope; the composition of the heavy fraction in such sediments is probably altered. Variations of ferromagnetic contents in that case may be a result of a decrease in detrital iron in Fe_{gross} of the Late Würmian sediments, as well as changes of their granulometric composition with an increase of finer fractions more subject to dissolution. A substantial alteration of iron forms in boundary sediments Q_3^4 – Q_4 , indicated by the gross iron content in terms of abiogenic sediments, remained largely unchanged (K-13-4) and even increased down the section (K-13-5). In that respect, κ and J_n in the transient zone should be compared with variations of the ratio K_2O/Na_2O , which, according to Rukhin, is a measure of the sediment's "maturity". According to this study, a brief transport of clastic matter results in a higher Na content in the sediment than K content; a prolonged reworking of the seafloor causes dissolution of Na and reduces its concentration in the sediment. In cores K-13-4 and K-13-5 a transition from the Holocene to glacial Q_3^4 is clearly accompanied by a rise of the K_2O/Na_2O ratio, indicative of the degree of reworking on the basin floor. Transport and mechanical reworking of sediments thus also affect substantially the concentration of ferromagnetic minerals in the sediments of the continental slope. This factor and the previous one (iron sulfidization) are largely controlled by sea level fluctuations.

Several specific features of the variation of κ and J_n of sediments against their general background trend in the transient zone are remarkable. In both columns the portion of the core where natural remanent magnetization increases is above the interval where magnetic susceptibility increases, i.e., magnetic grains became oriented after deposition. During the Holocene a slight decrease in κ and J_n up the section is observed after their maximum at the base of Q_4 . This may be reflection of the specifics of the pyritization of the ferromagnetic component in various redox settings, or it may be a result of the mechanism of formation of orientational magnetization in the sediment.

In these "transient zones" of K-13-4 and K-13-5 the contents of basic rock-forming elements also vary: SiO_2 decreases toward the base of the zone; this is accompanied by a rise of Al_2O_3 , Fe_{gross} , MnO , MgO , and other values (Table 1). One of the factors responsible for these variations is a drop in SiO_2 (amorph.) content in the sediment; it is mainly represented by diatom skeletons. This is confirmed by direct determinations of SiO_2 (amorph.), the values of SiO_2 (amorph.) calculated from $SiO_2 - 4Al_2O_3^*$ [8], and micropaleontologic counts of valves per gram of dry sediment (see Fig. 2). Data recalculated for sediment with no SiO_2 (amorph.) show that the concentrations of most rock-forming elements are relatively constant along the core, while SiO_2 (amorph.), K_2O , Na_2O , S , CaO , P_2O_6 , and CO_2 vary in the transition zone. The variations of SiO_2 (amorph.) and CaO in the transition zone of these columns, combined with the results of observations of polished sections (presence of diatoms, sponge spicules, diagenetic calcite, and foraminiferal shells) generally match a previously determined pattern of the variation of these concentrations of biogenic component

*The baseline value of SiO_2 (amorph.), calculated after Lisitsyn [8], was set as the minimal value for each core.

in the sediment near the boundary between the Upper Pleistocene and the Holocene [2]. In the Sea of Japan, the sediments of the latest glaciation are enriched in CaCO_3 (while SiO_2 (amorph.) contents are low); in the Holocene carbonate concentrations drop (their preservation deteriorates), while the content of amorphous silica increases (a higher productivity of seawater). These variations of biogenic components are attributable to sea level fluctuations and changes in ancient oceanic conditions [2].

Fairly high correlations in variations of SiO_2 concentration and that of most terrigenous elements is observed in K-13-5 and K-13-2 columns (Table 2); for K-13-4 the correlation is somewhat weaker. Certain variations of correlation coefficients for the same elements between columns give some idea of differences in supply provinces and transportation routes of terrigenous material in the region. Low (<0.5) correlation coefficients of terrigenous element contents in some of the cores indicates a possible variation of supply sources of terrigenous matter over time. Mineral and chemical composition of the sediments fit in with this assumption. X-ray structural investigations indicate that the quartz-plagioclase ratio in sediments of the ancient part of the K-13-5 column is variable, decreasing to the bottom of the transition zone from 0.76 to 0.56 (Table 3). A detailed study of clay minerals in the surface sediment layer of the Sea of Japan by Kurnosov [5] confirmed Rateev's [12] theory of migration of the transportation zones and seafloor clay deposition areas for each of the terrigenous flow sources. According to Kurnosov, transport from the islands of Japan, Sakhalin, and the Asian part of the Eurasian continent is predominant in the northern part of the sea. Mixed-layer hydromica-smectitic minerals with a predominance of swelling packets is mainly washed down from Sakhalin, Honshu, and Hokkaido Islands.

Primorye Province and the eastern slopes of the Sikhote-Alin Range supply mainly hydromica and chlorite and subsidiary amounts of mixed-layer hydromica-smectitic minerals.

X-ray structural investigation of the K-13-5 core shows a rising hydromica concentration and a decline of smectite proportion toward the base of the transition zone as compared with the sedimentary top layer (see Table 3). A higher concentration of hydromicaceous minerals is observed also down the column, with a drop in the interval of 300-350 cm, where the proportion of smectite rises considerably. According to Kurnosov, this variation in the mineral composition of clays reflects an increase in the Late Würmian of the role of transport of material from the continent in the Primorye area and a reduced terrigenous contribution from the surrounding islands.

The moisture content and density of sediments, as well as other physical properties, experience variations in the transition zones of cores K-13-4 and K-13-5. The moisture content declines as we pass to lower glacial sediments Q_3^4 , while the density increases. It has been established [7] that the moisture content and volumetric weight of marine sediments are controlled by several factors: granulometric and material composition (CaCO_3 , SiO_2 (amorph.), C_{org} , and heavy mineral contents), the age of the sediment, etc. In these columns, a decrease of W and an increase of Δ down the section is associated with a drop in SiO_2 (amorph.) in Q_3^4 sediments; their granulometry becomes coarser, and the proportion of swelling packets decreases. The changes of these last three parameters are controlled mainly by sea level fluctuations and preparation and transport of matter to the continental slope.

Thus, as glacial sediments Q_3^4 are succeeded by the Holocene up the section in K-13-4 and K-13-5, both physical parameters (κ , J_n , W , and Δ) and the material composition of sediments (SiO_2 (amorph.), CaO , $\text{K}_2\text{O}/\text{Na}_2\text{O}$, Q/Pl , and smectite proportions) are changed.

The main cause of these variations was probably the change of sea level and subsequent alteration of sedimentation patterns on the continental slope. When the sea level was low, the influence of land erosion and predeposited material from the first sedimentation level was increased; during the Holocene, sediment was formed mainly by one-stage supply of suspended matter from land and its distribution in the basin. The variations of these parameters should not be directly correlated with sea level fluctuation: the relationship could be mediated through changes of the general paleoceanic setting in the basin and the physical and chemical deposition environments.

In column K-13-2, collected from the base of the continental slope near a canyon, an abrupt change of the physical properties of the sediment (moisture content, volumetric weight, and magnetic susceptibility) is seen at the top of the Holocene (0-35 cm). Oxidized sediment in this interval has a high moisture content (72%) and a low volumetric weight. A rare sampling for chemical analysis of the subjacent relatively homogeneous sedimentary bed (35-250 cm), which encompasses the Early Holocene, the Late Würmian, and the latter part of the Middle Würmian revealed no definitive compositional variations, except for a slight increase of the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio in the middle of the column. However, detailed diatom analysis indicates that the Holocene and the second half of the Middle Würmian have higher abundances of algal valves compared with the Late Würmian. Nor are there any important changes in the physical properties of this bed except for a low peak of sulfide sulfur content (ΔJ_n at the Q_3^4 - Q_4 boundary).

In core K-13-2 the variations of the physical properties and the chemical composition are more pronounced in sediments corresponding to the time of transition from the Middle Würmian interstadial Q_3^3 to the Early Würmian cooling Q_3^2 (see Fig. 2, interval 250-350 cm). Diverse granulometry and material composition are typical for the sediments of the Early Würmian cooling. The frequent interstratification of siltstone, pelite, and small gravel and

pebble inclusions against the background of a generally coarser sediment indicate that, during regressions, gravitational sedimentation processes were predominant in shaping the canyon's alluvial cone. This, in turn, intensified the influx of the coarse fraction of ferromagnetic minerals that were resistant to dissolution. Subsequent sea transgression during the Middle Würmian damped the gravitational accumulative factors and changed the material composition of sediments and their physical properties. Moisture content, density, and chemical composition variations in the sediments in the transitional zone of core K-13-2 are largely similar to fluctuations of these parameters in cores K-13-4 and K-13-5, discussed earlier. In addition, the proportion of SiO_2 (amorph.) also decreased toward the base of the transition zone, and concentration of CaCO_3 (diagenetic calcite) increased; the content of pyrite sulfur (based on chemical analysis of ΔJ_n data) increased, and so did the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio. The main source of variation in this column is probably also sea level change; because of its specific geomorphological location (near the canyon mouth) it resulted in a more intense gravitational accumulation during the Early Würmian regression.

Diatom investigations have thus identified, in three cores from the northwestern Sea of Japan, sediments of Riss-Würm Interglaciation, the Early, Middle, and Late Würmian, and the Holocene.

In two cores from the middle part of the continental slope the transition from the Late Würmian to the Holocene is accompanied by an increase in magnetic susceptibility, natural remanent magnetization, and moisture content; the material composition also changes. In the column from the base of the continental slope of Primorye Province near the canyon, due to sparse sampling, the variations of these physical properties and sedimentary components are most distinct in the interval representing the transition from the Early Würmian cooling to the Middle Würmian interstadial, i.e., an earlier sea transgression.

Overall, the changes in the physical properties and composition of sediments in the region were caused by glacioeustatic fluctuation of sea level and the related changes of the sedimentation settings and paleoceanographic conditions. A low sea level was conducive to land erosion; predeposited material from the exposed shelf made a considerable contribution to the sediment. At a high sea level, sediment was formed mainly by one-stage influx of suspended matter from land and its distribution in the basin.

Variations of κ and J_n are caused by changes in ferromagnetic component concentration in sediments, and can be due to: increased dissolution of detrital iron in the course of its sulfidization during sea regression and more stagnation conditions on the seafloor; intensified influx of redeposited material from the first sedimentation level, characterized by a depleted concentration of ferromagnetic materials when the sea stood at a low level; and an influx of coarse-grained ferromagnetic materials more resistant to dissolution during sea regression in areas geomorphologically predisposed to accumulation of gravity deposits.

An increased proportion of redeposited material during glaciations in the sediments of the continental slope is also indicated by a rise in the K/Na ratio in the sediment, i.e., their "maturity." Variation of the physical properties and material composition of sediments are probably also caused by an increased proportion of terrigenous material brought from Primorye Province as compared with the amount of material transported from surrounding islands during glaciations. This peculiar geographic structure of this marginal basin was responsible for the rise of SiO_2 (amorph.) and a decline of CaCO_3 concentration during sea transgressions (at the middle of the continental slope these changes are especially obvious during the last transgression).

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The relationships between fracture systems on the floor of the Pacific Ocean and fields of Fe—Mn concretions, and between the manganese content of sediments and the distribution of faults in the Atlantic Ocean, were examined. The information obtained supports the view of N. M. Strakhov that volcanism has little effect on the formation of Fe—Mn concretions and crusts on the ocean floor.

The problem of the origin and source of supply of manganese (and other macro- and microelements) on the ocean floor, and its involvement in ore formation, has an extensive history and has long been discussed on the pages of journals and monographs.

Strakhov [9-11 etc.] and a number of Soviet and foreign investigators concluded that Mn, Fe, etc. elements have a mainly continental origin and are carried to the sea by rivers from various types of weathering mantles developed in their drainage basins.

According to Strakhov, the geochemical process in the ocean is mainly physical and is controlled by the mechanical transport and fractionation of soluble and solid phases supplied from shore. It is complicated by biogenic sedimentation (calcium and magnesium carbonate, organic matter, silica), and to some extent it is physicochemical (coagulation and precipitation of Mn and Fe from bottom waters and their absorption of microelements). As a result, this process leads to the formation of ocean basin Fe—Mn concretions, forming fields of colossal size.

A sharply different point of view was expressed by Lisitsyn and his coworkers [5] who believed that the principal role in the geochemistry of manganese in the oceans belonged to volcanism, which controls its distribution and accumulation in sediments and ores. As these authors note, an objective examination of new data indicates substantial errors by Strakhov on the question of the amount and composition of material supplied to the oceans by rivers.

In the work cited, Lisitsyn et al. write that the quantity of material supplied by river currents (as implied in Strakhov's papers) has for many years been greatly exaggerated (by 8 or 10 times). Recently obtained data indicate a sharp separation at the river-ocean barrier. Most of the material (90% or more) is deposited at the river mouth, without entering the ocean, and forms deltas and submarine fans. The thickness of the fans, based on geophysical data, reaches 12-15 km; depositional processes here are characterized by high rates, leading to formation of deposits with special properties. These colossal masses are compensated by an isostatic subsidence of the crust, which assures the accumulation of such high thickness of sediments in a single place.

From this paragraph it can be surmised that Lisitsyn had information which was not available to Strakhov, and that this made it possible for him to comprehend anew all the aspects of sedimentation in the various parts of the oceans and to resolve the question of the source of manganese and a number of other elements in the formation of Fe—Mn concretions and other mineral resources on the ocean floor. We hasten to note that Strakhov was aware of the views put forward by Lisitsyn. In a number of articles and monographs he discussed these ideas of Lisitsyn, pointing out their errors.

In our opinion, Strakhov has persuasively shown that the decisive mechanism of sedimentation of the material entering the basin of deposition was, is, and always will be grain-size and geochemical fractionation. According to Strakhov, volcanism has no important effect on the balance of manganese (or iron, or many other elements) in the ocean.

In a paper devoted to the manganese balance in the oceanic sediment cycle, Volkov [1] confirms, on rather strong evidence, the leading role of continents as suppliers of manganese to the oceans, as described by Strakhov.

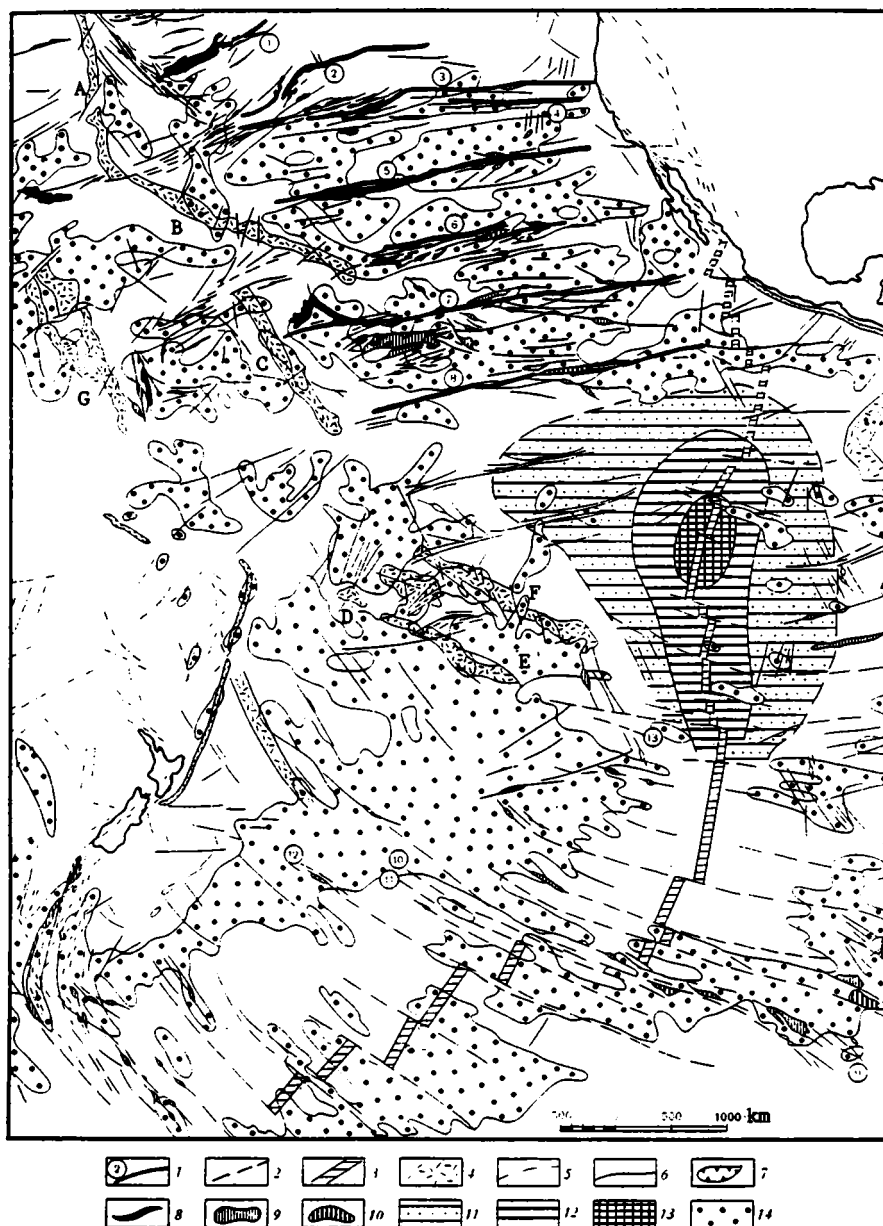


Fig. 1. Map showing distribution of fields of Fe—Mn concretions on the floor of the Pacific according to [15] together with faults according to [7]. 1) East—west faults (1, Chinook; 2, Surveyor; 3, Mendocino; 4, Pioneer; 5, Murray; 6, Molokai; 7, Clarion; 8, Clipperton); 2) faults connected with the East Pacific rise (9, Eltanin; 10, Heezen; 11, Tharp; 12, Udintseva; 13, Kurchatova); 3) faults along the crest of the East Pacific rise and its extension; 4) linear zones of deep penetration; 5) faults of the continental margins and island arcs; 6) other faults; 7) deep marine trenches; 8-9) basins (8, more than 5500 m deep; 9, 3500 to 5500 m deep); 10) submarine ridges; 11-13) areas of exhalation (according to [9]) (11, weak; 12, medium; 13, maximal); 14) fields of Fe—Mn concretions [15]. Zones of deep penetration: A, Emperor; B, Hawaii; C, Line; D, Cook; E, Tubuai; F, Tuamotu; G, Gilbert.

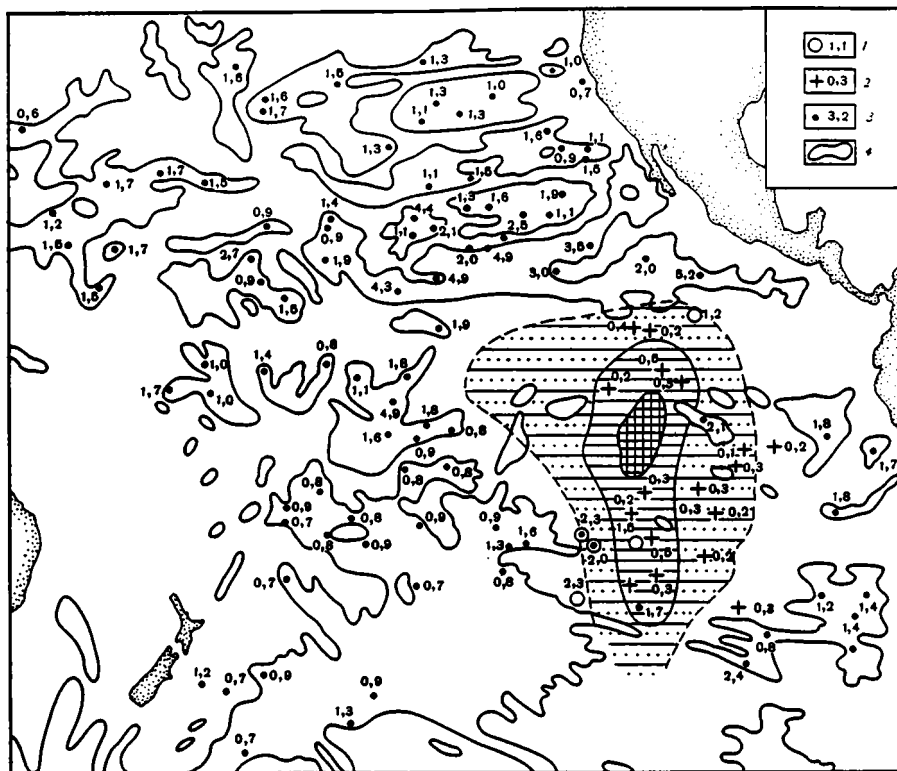


Fig. 2. Relationship between manganese and iron in Fe—Mn concretions. 1-3) magnitude of Mn/Fe (1, in Fe—Mn concretions; 2, in metalliferous sediments; 3, in concretions in the upper part of the metalliferous sediments); 4) field of Fe—Mn concretions. Other conditions as shown on Fig. 1.

The present paper also presents information which leads to resolution of the questions, hitherto considered debatable, of the primary and secondary sources of the manganese that participates in sedimentary Fe—Mn ore formation.

Relationship between Fe—Mn Concretion Fields and Fracture Systems. The formation of Fe—Mn concretion fields and very thin deep-water, fine-grained pelagic sediments enriched in Mn, Fe, and other elements, as a result of geochemical and grain-size fractionation, is one of the most remarkable features of oceanic lithogenesis, first recognized by Strakhov [9 etc.]. Distinguishing features include a huge size relative to the basin, an extremely low ratio between the area of supply and the area of sedimentation, the rather small amount of biologic productivity in the upper layers of the water, considerable metamorphism of newly formed biogenic material and its extremely low content in the sediments (C_{org} 0.1-0.2%). Deepwater red clays characterized by a high Eh (+500; 550 mB), which emphasizes the oxidizing conditions, are widespread on the ocean floor. Concretions in the ocean basin have various shapes and sizes. They differ in the nature of their surfaces and in other parameters. Also important is the particular ore mineral assemblage present in the sedimentary (hydrogenic) concretions and crusts. These include vernadite, asbolane, asbolane-buserite, buserite-I, buserite-II, and a number of other minerals with a far less fragment occurrence [14].

Concretions and crusts in the pelagic zone always contain manganese and iron as principal elements, although their ratio is not constant and varies widely. They are generally considerably enriched in microelements: the total content of nickel, copper, and cobalt sometimes reaches 5-7% [2].

Pushcharovskii and his coworkers [7] have studied a number of fracture systems in the Pacific Ocean, most of which are concentrated in the eastern half.

1. A system of major east—west faults (Mendocino, Murray, Molokai, Clarion, Clipperton, and others) that occupy the northeastern part of the ocean basin. These faults have a considerable extent (up to 3000 or 4000 km). The width of the fault zone reaches 100 miles and sometimes even more. They have complex structures, and contain narrow basins, ridges, banks, and scarps. The latter locally reach 2-2.5 km in height with 30° slopes, which suggest considerable vertical movement. The authors believe that the major faults are not deep-seated, and therefore do not

represent zones of deep penetration. Volcanic mountains here are typically very small, and show no connection with the faults.

2. A system of fault zones located in the southeastern Pacific Ocean (Menard, Heezen, Eltanin, Academician Kurchatova, etc.). Unlike those in the previous system, they are characterized by relatively simple patterns. The strike of the faults in this system is related to the East Pacific rise (according to [7], the East Pacific and South Pacific rises), although they generally occur beyond their limits.

3. A system of faults representing all the faults extending along the crest of the East Pacific rise (EPR). They are part of the oceanic rift systems of the world.

4. A system of deep-seated faults (a zone of penetration) extending along linear volcanic ridges (line islands, Hawaiian Islands, Emperor seamount, the Gilberts, Cook Islands, etc.). They are basically Cenozoic in age. The main volcanic ridges of this system strike northwest, which, along with other data, suggests structural autonomy.

The areal relationship between fields of Fe—Mn concretions [15] and deep-seated faults [7] in the Pacific is shown on Fig. 1. This comparison is convincing evidence of the convergent distribution of the Fe—Mn concretion fields and major east—west faults, as well as with the fault systems located in the southeastern Pacific. It is most likely that the restriction of Fe—Mn concretions to these major fault zones is related to the high relief of the faults, which promotes the turnover of bottom waters due to current action.

At the same time, fields of Fe—Mn concretions are clearly not correlated with deep-seated fault zones with high penetration, even though these fault systems would have been excellent pathways for the introduction of volcanic manganese. In a similar situation are concretion fields in the northern part of the East Pacific rise, the Galapagos rise, and other active ridges, where there are only local manganiferous or ferriferous (nonmanganiferous) crusts, or those practically devoid of iron, in close association with nontronite-celadonite clays. Typically, hydrothermal manganese deposits, unlike hydrogenic Fe—Mn concretions, are characterized by a stable todorokite-birnessite association [4, 12, 13, 17, 18].

Thus, Fe—Mn concretions in the pelagic zones of the ocean differ in mineralogical composition from hydrothermal deposits localized on active ridges. Moreover, the fields of Fe—Mn concretions do not coincide with the active ridges, but instead cut across them. In addition, a clear-cut disparity has been established between the ages and compositions of Fe—Mn concretions and metalliferous sediments, in the upper part of which they were formed (for example, the Bauer depression and others). A connection between the magnitude of the manganese modulus (Mn/Fe) and active hydrothermal zones located on the East Pacific ridge is also lacking (Fig. 2). Even more problematic is the relationship between Fe—Mn ore formation in hemipelagic areas of the ocean and volcanism, as pointed out in [5].

A great many authors who have studied aspects of Fe—Mn ore formation in the frontal zone of island arcs and in hemipelagic zones have shown that it takes place in sediments at a relatively high rate of deposition in the upper relatively thin (10–15 cm) part of the oxidized layer (Eh +400; +450 mB). It is underlain by much thicker reduced sediments. The formation of concretionary ores and crusts, associated with processes of diagenesis, as theorized by Strakhov in [8], is based on a single mechanism. Suspended forms of Mn, Fe, and other elements introduced into the basin are reduced as an effect of organic matter in the sediment, are transformed into soluble forms, and accumulate in muddy water. Interchange between muddy and bottom waters leads to some depletion of a few of the mobile elements (Mn and Fe), such that conditions are created for the diffusive flow of the elements into a type of sediment, bottom water, where Fe—Mn nodules and crusts are formed.

Concretion ores at the margins of the ocean are weakly developed nuclear forms. They are generally irregular in shape and range in size from 1 to 2 cm, rarely a bit larger, and are usually composed of volcanic ash or rock, rounded lithified sediment, etc. They are encrusted with iron hydroxides (8–10%) with smaller amounts of manganese hydroxides (4–6%); the manganese-to-iron ratio is usually less than one. The ore layer is not thick, and the insoluble residue is frequently quite high, commonly reaching 75%. The content of minor elements in ores of the frontal areas of island arcs is small (Ni, 0.16–0.19%; Cu, 0.08–0.115%; Co, 0.048–0.060%), but it is greater by an order of magnitude than in the sediments around and beneath the concretions and in deposits associated with volcanic processes. The sediments surrounding and underlying the concretions contain a number of authigenic minerals (iron sulfides, glauconite, calcitic rhodochrosite, etc.), indicating that typical diagenetic processes prevailed in the sediments in this zone [2, 9, 10, etc.]. Data presented by Glagoleva [3] suggests a gradual transition in composition of Fe—Mn concretions from hemipelagic to pelagic areas, in which there is a considerable reduction in the amount of reactive iron taking part in the ore formation, and an increase in the degree of oxidation and the amount of manganese. A similar picture is found along profiles extending away from major island systems. Near these the Fe—Mn concretions, as in hemipelagic zones, contain a greater amount of iron and terrigenous components, with manganese in a secondary position. Away from the islands, manganese increases sharply, it is more and more oxidized, and the iron content sharply decreases.

The fault configuration in the margins of the Pacific also does not fit the distribution of Fe—Mn concretion fields.

TABLE 1. Average Values for Mn/Fe and the Content of Minor Elements in Fe—Mn Concretions of the Pacific (I) and Atlantic (II) Oceans at Various Latitudes [16]

Latitude, degrees	Mn/Fe		Ni+Cu+Co	
	I	II	I	II
60—40	1,4	0,78	0,78	0,74
40—20	1,6	0,7	1,32	0,69
20—0	2,4	0,86	1,98	0,60
0—20	1,3	0,7	1,20	0,83
20—40	0,99	1	1,04	0,87
40—60	1,11	0,6	1,01	0,59
60	0,6	?	0,71	?

Mazarovich [6] examined in detail the location and type of faults in the north-central Atlantic Ocean. According to his data, the following basic types of tectonic faults are found between the equator and 40°N:

1. Large east—west faults (very complex) that transect essentially all structures in the ocean.
2. A system of tectonic faults associated with linear structures of the mid-Atlantic ridge.
3. Faults of the passive continental margins of the Atlantic.
4. A system of tectonic structures the formation of which is related to horizontal tectonic layering of the oceanic lithosphere.

Upon comparing the fault systems found on the bottom of the Atlantic with Fe—Mn concretion fields, a picture is found that is generally similar to that in the Pacific. The Fe—Mn concretion fields also coincide with major east—west faults; in this case they are not everywhere, but only in individual relatively large areas. It is likely that these areas have a sharply expressed tectonic heterogeneity in their relief, regulating bottom currents and producing a more intensive resupply of soluble and suspended material derived from the continents. The rest of the faults, including active ones which are associated with typical hydrothermal ore deposits, such as manganese and iron incrustations, iron—copper—zinc sulfides, etc. [4, 7, 18], are not associated with Fe—Mn concretions.

The total amount of concretions in the Atlantic is known to be much smaller than in the Pacific. A number of investigators have interpreted this situation to be the result of a greater rate of accumulation of terrigenous materials in the Atlantic, supplied by streams from the continents [4 and others]. Atlantic concretions differ from those in the Pacific in having a greater amount of iron and a lower content of nickel, copper, and cobalt [16]. The data presented in Table 1 show that the highest values for the ratio of manganese to iron and the highest content of the microelements indicated above are limited to concretions found in the north equatorial zone (0—20°N) of the Pacific Ocean and in the south Atlantic (20—40°S), which in our opinion is impossible to explain by introduction of volcanic manganese from active fault zones.

Moreover, the high iron content and lower amount of microelements (nickel, copper, and cobalt) in concretions and crusts in the Atlantic compared to similar forms in the Pacific are quite readily explained by Strakhov's concept of varying intensity of fractionation of material supplied from drainage basins on the continents, depending on the size of the depositional basin.

Relationship between Manganese Content in Oceanic Sediments and Fields of Fe—Mn Concretions. In [5], a considerable amount of attention was paid to the distribution of Mn in surface sediments of the Atlantic and Pacific. These authors believed that, on the basis of maps they compiled of the distribution of manganese in oceanic sediments, the following conclusions could be drawn: 1) the manganese concentration in oceanic sediments is much higher than in sediments of interior (Black) or marginal (Bering and Okhotsk) seas, and 2) the highest concentrations of manganese tend toward active mid-oceanic ridges.

We note that Strakhov [9-11 etc.], having studied mechanisms of increase in content of Fe, Mn, P, Co, and other elements (and not just manganese alone) in pelagic sediments of the larger seas and oceans in comparison with smaller continental basins, concluded that such enrichment was primarily associated with fractionation of fine suspensions introduced from the continents. He found that the larger the basin and the longer the transportation of the particles in suspension, the greater the possibility of subdivision of the suspension and the more distinct the enrichment of pelagic muds in the elements mentioned. Strakhov noted that muds of the Arctic basin were notably enriched in Mn, Fe, P, and other elements compared to Black Sea or Sea of Okhotsk muds, while Atlantic muds were even more enriched than similar deposits in the Arctic basin. Finally, sediments of the pelagic zones of the Pacific contain more Fe, Mn, P, Co, and other elements than muds of the Atlantic. We would add that geochemical and mechanical

TABLE 2. Hydrothermal Deposits Found on the Mid-Atlantic Ridge, from [17, 18]

No.	Locality (coordinates)	Mineral	Mn	Fe	Ni	Cu	Co	Type of occurrence
3	Crest (45° N), floor of rift valley	Goethite, montmorillonite, manganese hydroxides	0,03—0,7	2,5—8,5	20—370	25—167	—	Sediments
5	Crest (36° N)	Fe-montmorillonite, nontronite, todorokite	2,9—8,3	14,5—28,4	28—325	49—135	3—27	Red, yellow, and green encrustations
6	Crest (26° N)	Birnessite, manganese nontronite, todorokite	9,6—27,0	0,79—26,8	2—275	46—275	—	Fe-Mn concretions
7	Crest (25°48' N, 44°59' W)	Birnessite, todorokite	38—52	0,01—0,11	50—790	11—119	14—25	Crusts
8	Crest (24°12' N)	Nontronite	0,7	32,4	100	100	100	Seams
9	Crest (23°36' N)	Pyrite, chlorite, quartz	—	—	—	—	—	Grains and veinlets of sulfides, quartz veins
10	West flank (23°N)	Quartz, chlorite, pyrite, chalcopyrite	—	—	—	—	—	Quartz in goedes (euhedral) and veins (massive), grains of sulfides
11	Crest (22°30' N, 45°W)	Same	—	—	—	—	—	Greenstone breccia with sulfide grains
12	Crest (16°47' N, 46°23' W)	Todorokite	Много (?)	Мало (?)	—	>1000	—	Crusts
13	Crest (12°48' N, 44°47' W)	Quartz, chlorite, pyrite, chalcopyrite	—	—	—	—	—	Sulfide grains, quartz veins in greenstone breccia
14	Equatorial zone (11°N)	Manganese oxides	—	—	—	—	—	Crusts
15	Equatorial zone (0°)	Pyrite, chlorite	—	—	—	—	—	Grains and veinlets of sulfides in greenstone
		Chalcopyrite, pyrite, pyrrhotite	<0,1	32	—	5·10 ⁴	—	Grains and veinlets of sulfides in metabasalts
		Same + goethite	0,05—0,19	29—51	90—270	35—390	27—75	Sulfide concretions, grains and veinlets of sulfides in metabasalts

Note. Mn and Fe content in percent; Ni, Cu, and Co, 10⁻⁴ %.

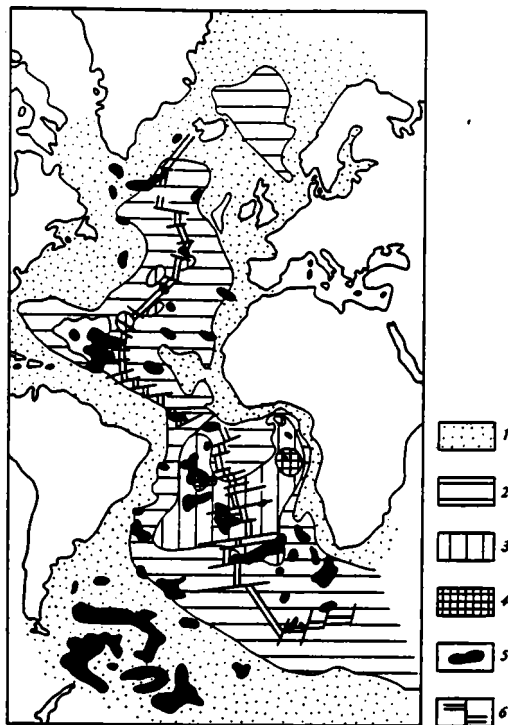


Fig. 3. Map showing the distribution of Mn in sediments of the Atlantic Ocean, from [5], combined with the distribution of fields of Fe—Mn concretions, from [15]. Manganese content, % (in siliceous, carbonate-free material): 1) < 0.2; 2) 0.2-0.5; 3) 0.5-1.0; 4) 1.0-3.0; 5) fields of Fe—Mn concretions; 6) mid-oceanic ridge.

fractionation would explain differences in composition of Fe—Mn concretions of hemipelagic and pelagic zones with in the same ocean basin, differences in composition of Fe—Mn deposits in lakes, seas, oceans, etc.

In our view, it is important to examine the position set out by Lisitsyn and his coauthors that increase in manganese content in the surface layer of oceanic sediments is restricted active mid-oceanic ridges. In order to resolve this question, we set up a scheme by which the distribution of manganese in surface sediments of the Atlantic Ocean [5] and Fe—Mn concretion fields [3] are compared. To this diagram we added the position of the mid-Atlantic ridge and the data of Rona [17, 18], presented in Table 2, on hydrothermal deposits found in the upper part of sediments in the Atlantic. It can be seen from this map that authors who assert that sediments with a high manganese content are generally restricted to active mid-oceanic ridges are in error. The map (Fig. 3) shows that sediments in the axial part of the mid-Atlantic ridge are associated with average or lower manganese content (< 0.2%). The fields of Fe—Mn concretions are totally unrelated to sediments characterized by a very high manganese content. According to data of Rona [18], out of 15 hydrothermal deposits currently known on the Mid-Atlantic Ridge (Table 2) only five have manganese or iron deposits. All of them (including the remaining ten that have no such deposits) are located in the northern half of the Atlantic, while most of the fields of Fe—Mn concretions are located in the southern half. Moreover, it is apparent on the map (Fig. 3) that the concretion fields do not coincide with active faults and vice versa (as in the Pacific), but considerably more frequently cut across them, which suggests that they are dissimilar in origin.

The data presented confirm that there is no genetic connection between fields of Fe—Mn concretions and systems of deep-seated faults, although the faults, by their presence, play a part as bridging channels for volcanic fluids involved in sediment- and ore-formation.

Also lacking is an unequivocal connection between concretion fields and the distribution of manganese in the sediments. In some cases concretion fields are actually located in sediments with a high manganese content, while in other cases, in sediments where it is practically absent or is present in minor amounts. Moreover, Fe—Mn concretion fields evidently do not correlate with hydrothermal deposits of manganese found on the Mid-Atlantic ridge (just as in the case of the East Pacific rise). In our view, this fact has only one explanation: the position of Strakhov on the fractionation of ore-forming and other elements during migration from the continents.

The material set forth above supports the view of those investigators who consider that a volcanic source of manganese and other elements involved in the formation of concretionary ores and sediments on the ocean floor does not have the great significance attached to it in [5].

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Two glass types develop in the interstices of continental and oceanic basalts: acidic glass with ore mineral inclusions, and a Fe—Mn-type with chlorophaeite. These form by secondary leaching that creates open spaces (2–5% of the basalt volume). It is assumed that significant amounts of matter are extracted in the initial alteration stages. Experimental leaching of chlorophaeite in sea water at 2 pH indicated that the synthetic sediment that forms when the solution is neutralized, according to its major (petrogenic) and trace element content closely approximates the composition of pelagic clays.

The influence of basaltic volcanism on the sediment- and ore formation on the ocean floor is presently well known. The extensive literature treats various aspects of this problem. Thus, Kossovskaya [3] formulated a theory on pelagic clay formation by secondary basalt alteration. Specific Fe-smectites, type minerals of the oceanic clays, in pelagic ocean areas are characterized by relative uniformity, reflecting the high level of uniformity of oceanic basalts, their source rocks.

Lately, a number of papers [1, 2, 4] theorized on the extraction of petrogenic and ore components through hydrothermal sea water circulation within basalt beds. The most detailed account of this concept appeared in Kurnosov's recent monograph [4].

Certain workers believed that extraction occurred at the contact between cooling basalts and sea water. Based on composition differences between basalt flow interiors and the overlying crust, Corliss [18] concluded that the depletion of basalts in a number of components was due to the interaction between sea water that infiltrates the cooling basalt flows and "residual fluids" (residual melt), enriched in such elements that could not enter lattices of the crystallizing minerals in the basalts. The lower basalt flow sections had been depleted in elements that were concentrated in ore-bearing sediments and Mn-concretions (Fe, Mn, Co, and the rare-earth elements). Many major experts on oceanic sedimentation and ore-bearing sediments have endorsed the Corliss theory [5, 18].

Obviously, even a brief review provides a hint of the complexities and varied role of basalts in oceanic sediment and ore formation processes. Based on numerous comparative studies of mineral alterations of continental and oceanic basalts, the present authors developed theories about the sequence of processes during the earliest basalt alteration stages and their impact on the pelagic sediment and ore genesis. According to these ideas, interaction between sea water and the cooling basalt flows under pelagic conditions results in a significant loss of petrogenic and ore components, due to leaching of the reactive Mg—Fe glass (chlorophaeite) from the interstices of crystallized basalts. New data are presented and certain already known facts, not yet adequately considered, are discussed. Hopefully, interpretation of these facts within the suggested theoretical framework will lead to a fuller understanding of the very complex problem regarding mobilization of basalt components during oceanic sediment genesis.

This study is based on study results of certain continental and ocean basalt types and also on the review of the extensive literature. Post-eruptive processes, studied in great detail in Devonian tholeiitic plateau basalts of the northern Timan area, led to formation of a reactive Mg—Fe glass (chlorophaeite) in interstices of incompletely crystallized basalts [8].

These processes had been identified in the large basalt flow exposures of the northern Timan and plateau basalts on other continents, related to various rock textures; such studies would be most difficult to perform in drillcores. The composition and texture of northern Timan basalts are very close to those of the oceanic tholeiites. It was important that their Mg—Fe(chlorophaeite) phase is well developed and available for study.

The oceanic basalts were studied in samples taken for the United States National Science Foundation (Cruises 32–34, DSDP), by A. G. Kossovskaya (Cruise 69), and in thin sections, provided by L. V. Dmitriev (Cruise 37). Young

TABLE 1. Chemical Analysis Data (microprobe results), in %

Oxides	Chlorophaeite				Interstitial glass			
	Timan [8]	Vitim plateau	Iceland [22]	drill- hole 304 DSDP	Timan	Iceland [22]	drillhole 396B DSDP [27]	
							sample 1	sample 2
SiO ₂	45,00	45,08	45,58	46,49	74,49	75,25	63,03	73,60
TiO ₂	0,05	Her	0,03	0,64	0,71	0,39	1,33	0,50
Al ₂ O ₃	6,13	6,20	5,57	3,27	12,74	13,49	14,08	14,91
FeO	28,65	19,96	24,48	28,10	3,22	1,50	5,57	2,61
(Total)								
MgO	7,28	6,88	10,69	9,78	0,06	0,01	1,53	0,37
CaO	2,71	0,67	1,46	0,94	2,52	0,69	2,12	2,24
Na ₂ O	0,09	0,02	0,03	0,45	2,86	3,67	5,94	5,73
K ₂ O	0,44	0,12	0,32	0,27	0,56	3,80	0,28	0,46
MnO	0,09	0,48	0,30	0,11	0,04	0,01	0,17	0,03
(Total)	90,44	79,41	88,46	90,05	97,20	98,81	94,05	100,45



Figure 1. Textural position of chlorophaeite and clay minerals in basalts. a- chlorophaeite (gray) in xenomorphic interstices; white-plagioclase; black-Ti-magnetite (N. Timan); nonpolarized light, 80× magnification; b-xenomorphic areas of leaching, involving pyroxene and plagioclase crystals (Tadzhur Rift), nonpolarized light, 30× magnification; c-secondary saponite (gray) in xenomorphic pore (Drillhole 332A, DSDP), nonpolarized light, 80× magnification; d- K-Fe clay mineral, in contact with talilitic glass and plagioclase crystals (Drillhole 332A, DSDP), nonpolarized light, 80× magnification; e- leached area, SEM-image (Tadzhur Rift), needle-shaped pyroxene and lath-like plagioclase crystals; f-primary gas cavity, SEM-image (great Treshchin Tolbachiksk eruption, Kamchatka).

basalts from the Tadzhur Rift were also studied in detail. These were sampled during the 9th Cruise of r/v "Academician M. Keldysh" with the help of POA "Paisis".

Basically poorly crystallized continental and oceanic basalts have been investigated; 80-90% of the volume was crystalline and possessed intersertal, tholeiitic and microphitic structures. Glassy basalts were not studied.

INTERACTION BETWEEN SEA WATER AND COOLING BASALT LAVA

In certain views, interaction between sea water and cooling lava flows is impossible for two reasons: the contact exists for a very short time and sea water can not easily penetrate the flow or pillow through the quickly forming glassy crust.

It is assumed that the time required for the cooling of basalt lava is sufficient for the chemical reactions to occur between reactive basalt components and sea water at higher temperatures and pressures. Data show that the last portion of the melt in a 14 m thick lava flow hardened only 13 months after the eruption [24]. The interior of the flow took four years to cool to a temperature of 100°C. Pillow lavas cool much faster. However, the central portions of large rock bodies retained melts for several days or longer. Therefore, it appears that the speed of chemical reactions at higher (c.400°C) temperatures increases by a few orders of magnitude. The speed of water diffusion across mineral boundaries also increases markedly. It has been shown recently that this speed increased 1000 times with a temperature increase from 34° to 300°C [21].

The rapidly forming glassy crusts are not insurmountable obstacles to water infiltration into the cooling lava flows and pillows. These crusts are instantly penetrated by fractures during contraction and they may further penetrate the cooling melt [23]. In one view, water penetration into the melt (transvaporization) in underwater eruptions occurs due the difference in the partial pressures of water vapor in the lava and in the enclosing medium [11].

The argument for the absence of an interaction between residual basalt lavas and sea water usually cites the "fresh" appearance of basalt samples, taken in axial areas of sea floor spreading zones. These basalts usually contain no altered reactive sideromelane glass and olivine. Does this mean that basalt alteration has not yet started? It is known that young pillow basalts, without indications of palagonitization, oxidation and similar alterations do contain fractures. Dark gray fields ("black front"), usually with higher concentrations of K and Fe [28, 29] developed along these fractures in the central portions of the pillows. The "black front" was noted in samples that dated less than one million years and displayed no other alterations [17].

These facts indicate that the alteration of crystallized pillow cores and interior parts of lava flows apparently starts very early, probably already during the interaction that occurs between the residual lava flow and sea water [18, 28].

CHLOROPHAEITE AND CLAY MINERALS IN THE BASALT GROUNDMASS

Chlorophaeite has been studied in detail in the Devonian northern Timan basalts [8]. The pseudoamorphous character of isotropic chlorophaeite was expressed by the presence of similar structural features, analogous to those found in the associated oxismectites. It has been concluded that chlorophaeite, this hydrated and partly oxidized glass originated as the liquate phase of the original effusive basalt melt. Due to its intensively hydrophile character, chlorophaeite contains a maximum 20% of molecular water. Within limits, hydration and oxidation do not alter its phase affiliation. For this reason, in the first approximation "chlorophaeite" is identical with "femic glass". Strongly hydrated and oxidized femic glass is transitional toward the colloid phase (chlorophaeite gel). This exists in northern Timan basalts but not in ocean basalts.

The composition of basalt groundmass was first studied in northern Timan basalts [8] that contain intersertal and microphitic structures. Interstices between pyroxene and plagioclase crystals in these rocks usually are filled with acidic glass, often with inclusions of powdery and skeletal ore minerals, as well as of pyroxene, plagioclase and other, unidentifiable mineral microlites.

Only relatively rarely has acidic glass composition been identified. The ore mineral inclusions are relatively large and unevenly distributed in the entirely fresh and transparent rose-brown colored glass (Table 1). In acidic glass (transparent type and glass clouded with inclusions) the interstices contain chlorophaeite or oxismectite in the same amounts as the ratio of the glass component. A portion of chlorophaeite forms in glass. Occasionally, it forms exclusively in glass. It also fills interstices between pyroxene and plagioclase crystals, clearly with a xenomorphic relationship with them (Fig. 1a).

The groundmass structure of oceanic basalts is tholeiitic or intersertal and essentially identical to continental analogs. The interstitial matter is basically glass, usually overflowing with microlites and powdery ore matter. In contrast with continental trap basalt types, the groundmass of oceanic basalts contain few large glass particles without inclusions. For this reason, there is still little microprobe data available on glass composition [27]. These analysis data and comparisons between the refractive indices of minute pure glass particles and that of Canada balsam (e.g., from thin sections of basalts, from the Tadzhur Rift and from Cruise 37, DSDP) suggest that this glass is mostly acidic in oceanic basalts that are 80-90% crystallized.

TABLE 2. Chemical Analysis Data (microprobe results) of Clay Minerals from Basalts, Drillhole 304 DSDP, Sample 15-1 (108-112 cm), in %

Oxides	Glauconitelike mineral	Greenish-brown smectite
SiO ₂	54,30	45,82
TiO ₂	0,21	0,02
Al ₂ O ₃	2,65	5,57
FeO	22,51	15,58
Total		
MgO	5,07	15,69
CaO	0,50	0,18
Na ₂ O	0,18	0,63
K ₂ O	7,99	0,36
MnO	0,02	0,18

TABLE 3. Chemical Analysis Data (microprobe results). Newly Formed Phase, Dark Basalt Halo, Tadzhur Rift (sample 1093/3), in %

Oxides	1	2	3	4	5	6	7
SiO ₂	40,20	39,80	43,80	48,38	38,20	41,75	22,31
TiO ₂	0,07	0,37	0,07	0,02	0,09	0,11	0,10
Al ₂ O ₃	4,99	5,64	5,47	9,97	6,00	5,84	2,90
FeO	31,47	31,14	30,38	27,71	32,43	29,82	42,83
Total							
MnO	0,02	0,00	0,01	0,00	0,00	0,01	0,18
MgO	9,76	9,87	7,39	4,14	8,31	7,99	1,94
CaO	0,58	2,09	0,53	0,76	0,48	0,69	0,25
Na ₂ O	0,44	0,32	0,59	0,38	0,54	0,22	2,16
K ₂ O	2,37	2,69	3,73	5,98	2,65	4,20	0,96
Total	90,18	91,72	92,06	95,48	88,86	90,82	73,63

Note: isotropic yellow matter, in pore rim; 2) same, interstitial matter; 3) green isotropic matter, interstitial matter; 4) slightly birefringent yellow substance, interstitial matter; 5) yellow, isotropic matter, rim of the previous substance; 6) slightly birefringent yellow substance, interstitial matter; 7) red isotropic substance, interstitial matter.

TABLE 4. Trace Element Concentration in Basalts (first value) and in Chlorophaeite (second value), ppm

Sample No.	Ba	Sr	B	Sn	Zr	Pb	Zn	Cu	Cr	Ni	Co	V	Ge	Sc
72-82	240	290	2,0	1,7	120	6,6	130	140	46	33	42	18	1,5	27,0
	340	170	7,2	6,1	420	9,7	64	190	8	41	52	65	0,6	4,8
128-79	60	250	2,8	2,2	115	5,1	160	190	54	36	48	210	1,7	12,0
	120	210	10,0	7,2	320	11,0	140	290	21	28	65	190	0,6	14,0
18-83	185	460	2,7	1,1	170	6,6	130	200	54	28	48	230	1,6	23,0
	250	290	6,7	2,3	300	19,0	150	250	16	68	68	77	0,5	7,1
48-82	95	270	2,8	2,1	55	7,2	140	120	80	52	50	180	1,8	6,5
	260	130	9,1	8,1	87	4,3	99	120	18	42	48	200	0,7	4,4
18-82	64	250	1,7	1,1	87	4,8	95	100	110	70	51	210	1,3	17,0
	57	107	4,6	2,1	110	5,5	95	130	19	180	85	140	0,9	5,8
120-79	60	290	2,0	1,7	120	3,9	200	120	88	46	52	200	1,1	19,0
	120	160	11,0	3,9	190	6,4	130	160	38	140	100	210	1,0	23,0
14-82	94	260	1,6	0,9	65	3,4	98	110	130	78	45	190	1,3	9,5
	370	82	4,4	2,3	94	4,8	85	240	15	110	84	105	1,5	6,0
15-82	77	220	2,0	1,3	80	3,2	120	98	140	80	53	210	1,3	11,0
	96	82	5,2	2,7	100	4,5	79	210	19	200	105	170	1,4	11,0
325-80	200	420	5,8	2,4	170	6,6	120	180	29	23	42	170	1,5	27,0
	190	235	7,8	4,0	330	19,0	110	210	13	22	53	150	0,8	15,0

The groundmass of oceanic basalts with relatively acidic glass usually contains typical clay minerals: high-Fe, high-Fe, high-K, high-Mg-varieties, practically without any K content [17, 19, etc]. In the groundmass they occur in the same textural patterns, with interstitial glass groundmass and encompassing crystal phases such as also chlorophaeite in continental basalts (Fig. 1a, c, d). Parts of the rock in the "dark zone", along contraction fractures, include

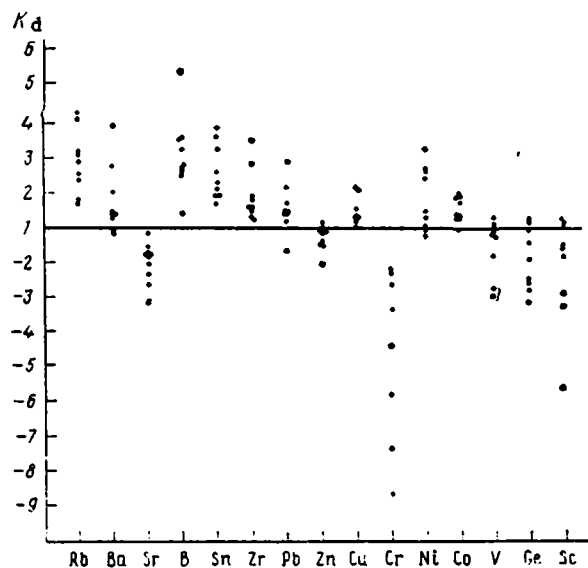


Fig. 2. Distribution coefficients (K_d) of trace elements between basalts and chlorophaeites, formed from basalts.

TABLE 5. Chemical Analysis Data of Chlorophaeites, Leached Chlorophaeite and Synthetic Sediments, Timan, in %

Oxides	Chlorophaeite, sample 18-83	Leached chlorophaeite, sample 18-83	Synthetic sediment			
			18-82	18-83	25-83	18-83*
SiO ₂	45.00	40.73	5.34	7.31	4.91	9.11
TiO ₂	0.05	None	0.91	0.01	0.01	None
Al ₂ O ₃	6.13	5.31	6.48	8.55	1.97	1.38
FeO	28.65	32.64	12.75	19.43	8.10	88.72
Total						
MgO	7.28	7.78	31.61	30.96	42.70	0.51
CaO	2.71	1.48	1.27	1.45	0.42	0.46
Na ₂ O	0.09	0.27	0.00	0.05	0.92	0.08
K ₂ O	0.44	0.37	0.04	0.05	0.06	0.10
MnO	0.09	0.14	0.14	0.25	0.10	None
Total	90.44	88.70	57.64	68.06	59.19	100.36

*Solution neutralized by sea water.

concentrations of mostly K—Fe—clay minerals; the rest of the rock volume usually is taken up by Mg-smectite. This fixed relationship is well known and has been widely described in the literature [17, 19, 20, 25, 26].

The groundmass of oceanic, especially of young basalts often encloses zones, the contours of which have been defined by the crystal shapes of the surrounding minerals and interstitial glass (Fig. 1b). The outlines of such fields, their dimensions and structural positions totally conform with the shapes of newly developed clay mineral formations in oceanic basalts, or with chlorophaeite outlines in continental basalts.

INTERSTITIAL VOIDS DUE TO LEACHING

At least three theories have been discussed in the literature on clay mineral formation in oceanic basalt groundmass with secondary alterations.

1. Many workers [4, 26] consider clay minerals in basalt groundmass as replacement products of interstitial glass. The initial glass composition is usually not noted. It is often assumed that the glass in the interstices is completely replaced by clay minerals. Therefore, the type of the original glass in the groundmass from which the clay minerals developed is uncertain. Occasionally, researchers have disregarded clearcut composition differences between residual (interstitial) and surface-hardened sideromelane glass [4].

TABLE 6. Average Values of Trace Element Concentration in Basalts (A), Chlorophaeite (B) and Synthetic Sediment (C), ppm values

Sam- ple No.	phase	E	Zr	Sn	Pb	Zn	Cu	Cr	Ni	Co	V	Sc	Mn *
18-82	A	1,7	87	1,1	4,8	95	100	110	70	51	210	17	0,31
	B	4,6	110	2,1	5,5	95	130	19	180	85	140	5,8	0,03
	C	64	680	10	18	150	130	50	280	156	176	48	0,28
18-83	A	2,7	170	1,1	6,6	130	200	54	28	48	230	23	0,21
	B	6,7	300	2,3	19,0	150	250	16	68	68	77	7,1	0,09
	C	80	600	12	38	200	160	13	190	130	170	28	0,50

*Mn values in percentages.

TABLE 7. Average Values of Certain Trace Elements in Pacific Ocean [1] and Synthetic Sediments, ppm values

Element	Sediment		
	metallogenic	pelagic	synthetic
Cu	841	387	145
Zn	422	248	175
Pb	152	89	23
Ni	841	182	235
Co	279	105	143
V	448	154	173
Zr	510	201	630
Sc	40	27	33

Only a few papers attempted to theorize on the composition of a hypothetical primary glass in the groundmass. Thus, Scott and Hajash [28] reviewed the likely chemical evolutionary process of the residual oceanic lava melt that determined the interstitial glass composition.

The predominantly interstitial position of clay minerals in the oceanic basalt groundmass is in good agreement with the assumption that the minerals were replacement products of residual glass. However, as noted, glass of a more acidic composition and with numerous ore mineral and microlite inclusions commonly occurs and sometimes predominates in the basalt groundmass. This glass usually is unaltered in young basalts and the contacts toward isolated clay minerals are sharp. Consequently, if the clay minerals formed from glass, not one but two glass types must have existed in the oceanic basalt groundmass. This does not contradict our theory [8] of the residual liquid-origins of the Mg—Fe-glass (chlorophaeite).

2. The theory that clay minerals in the basalt groundmass do not replace glass but formed from solutions in original interstitial pores, named "miarolitic cavities" [17, and others] is also widespread. Numerous pores, not completely filled by clay minerals do occur in the groundmass of very young, "fresh" oceanic basalts (e.g., in Red Sea- and Tadzhur Rift zone basalts, and of those of the Mid-Atlantic Ridge spreading zone). The void shapes were determined by the outlines of the adjacent igneous minerals (Fig. 1b). The basalts encountered during Cruise 37, DSDP, included empty voids and those, partly or completely filled by clay minerals.

We believe that the voids in the oceanic basalt groundmass are primary features, formed through degassing. Pyroxene, plagioclase and ore minerals are often very common in them (Figs. 1b, d). The mineral composition is identical in the basalt interstices and in the pores. Did these igneous minerals crystallize in gas cavities? It should be noted that the rock-forming minerals in the basalts (monoclinic pyroxene and basic plagioclase minerals) are typical magma minerals; they crystallize only from melt. In addition, should these minerals be able to crystallize in a gaseous medium, an effective supply of the required mineralizing substances may not be assumed through gas that becomes highly rarefied at high (c.1000°C) temperature.

In our view, the pores in question could not have formed during crystallization of the basalt melt. In the past, certain components of the residual melt had been removed at locations where the pores today occur.

One possible way to remove the residual melt has been discussed [13]. The authors admitted that the residual melt remains mobile even after crystallization of the igneous minerals has been completed. In this view, the remaining melt became segregated and was injected into earlier formed gas vesicles, due to the "filter-pressing effect"; the pressure caused by gas components, concentrated in the residual melt. After being vacated by the melt, gas pockets remained behind at such locations. It should be noted, however, that segregation vesicles [27], partly or completely filled by melt are relatively rare in oceanic basalts and the interstices (empty, or partially filled by secondary minerals) are most

common. In addition, rock-forming minerals crystallize when the cooling basalt melt is highly viscous [10]. The residual melt would have been highly viscous and its removal through the crystal lattice structure could not have occurred without destruction of the lattice.

No mechanism that may be responsible for primary formation of "miarolitic cavities" is presently known. It is more logical to assume that the interstices are secondary voids, formed through the leaching of reactive components that had been deposited earlier from the residual melt.

3. We assume that the interstices originally were spaces where metastable Mg—Fe glass (chlorophaeite) had been segregated; this was the differentiation product of the solidifying melt [8]. The Mg—Fe liquate is separated from the melt at the start of its crystallization. For this reason, it became intertwined with minerals of magmatic origin. The segregated femic liquate was isolated from the melt matrix by a tension surface. According to Redder [7], free diffusion of components does exist across this interface, and its results in a simultaneous equilibrium crystallization of the igneous minerals both in the liquate and in the matrix melt. As observed, the composition difference between the liquate and the groundmass may influence only the quantitative relationship between the isolated phases.

What is the difference between the interstitial voids and the primary gas vesicles in the basalts? The vesicles are not always rounded, sometimes have a very irregular, often multichambered shape. Usually they are separated from the groundmass by a combination of spherical surfaces, including concave ones. As an example, in the highly vesicular basalts of the Great Treshchinii (Fracture) Tolbachiksk effusives the numerous voids have a very irregular shape. However, no minerals of magma origin occurred in these gas pores and glass formed the bounding surfaces (Fig. 1f). A characteristic feature of the leached interstitial voids is their distinct interrelationship with the shapes of surrounding minerals of magmatic origin. Unfortunately, these features are not always clearly visible in petrographic thin sections. Crystals of the igneous minerals in the interstices are sometimes minute and brittle, crumbling easily during thin section preparation. Binocular, optical microscope and SEM studies of samples from young basalts of the Tadzhur Rift area identified minute pyroxene and plagioclase crystal growths, with well defined crystal faces in secondary interstices (Fig. 1e). In thin sections of the same samples these areas appear as isometric voids with irregular outlines, easily misinterpreted as gas vesicles. For this reason, identification of leached voids in petrographic thin sections must be confirmed by binocular microscopic studies of the samples.

CHLOROPHAEITE IN OCEANIC BASALTS

In the absence of leaching agents, as sea water, unaltered chlorophaeite in massive continental basalts is preserved for a long time and therefore is common in such rocks [8]. Chlorophaeite is almost always destroyed in oceanic basalts through leaching or decomposition. Even individual finds of this phase are therefore very important in oceanic basalts.

A fairly reliable chlorophaeite find occurred only in basalts of drillhole 304, DSDP [9]. Its color, glassy appearance, refraction index and isotropic character indicates a practical identity with chlorophaeites in continental basalts. The chemical composition values of oceanic and continental chlorophaeites are also close (Table 1). Chlorophaeite in basalts of drillhole 304 DSDP typically occurs in interstices but is also found in drop-like formations that often are partially or completely enclosed in minerals of magma origin.

References in the literature to the presence of chlorophaeite in oceanic basalts for various reasons appear to be unsubstantiated. Thus, the K—Fe- and Mg-chlorophaeites, described by Baragar and others [14] appear to be substances that formed from or occur at the location of femic glass.

Basalt samples studied by us (drillhole 304 DSDP) do not always include unaltered chlorophaeite. Near the roof of the flow the basalt groundmass included glauconite—celadonite-like K—Fe minerals and also Fe-saponite (Table 2). These minerals developed in the same structural positions as chlorophaeite did in other basalt samples in the same lava flow; i.e., in interstices or droplike precipitates. This shows that secondary clay minerals either are replacement products of femic glass (chlorophaeite) or fill secondary voids that formed through leaching.

SEA WATER-CHLOROPHAEITE INTERACTION

Our ideas represent a specific, further development of those of Corliss [18]. In place of a hypothetical "residual fluid" of Corliss in our context the Fe—Mg glass has a liquation origin; chlorophaeite essentially is defined entirely by its position in the rock texture. We have shown that chlorophaeite is highly unstable in acidic conditions. It decomposes fast (within a few hours) in sea water, acidified by hydrochloric acid to pH = c.2: iron is lost at the start and the residual phase loses its color. Later, as acidic conditions turn to alkaline, chlorophaeite is completely leached and interstitial

voids form, similar to those in the oceanic basalt groundmass. Based on information from the thin sections, the rock-forming minerals and acid glass with enclosed ore minerals did not undergo alteration.

Bischoff and Seyfried [15] indicated that sea water at high (350–400°C) temperatures becomes a hydrothermal fluid with a pH of 2.5. Such acid solutions may form not only during a secondary heating of rocks, due to large-scale hydrothermal circulation of sea water in the basalt beds, but also in conjunction with the cooling of basalt lavas.

After their eruption, sea water circulates throughout the cooling basalt lava flows along contraction fractures that migrate behind the cooling front, directed toward the center of lava flows or pillows. Sea water apparently enters the lava through fractures and capillary openings. In the first case, the large water volumes that enter, warm up relatively slowly, while the water that penetrates the cooling lava through capillaries or diffusion, heats quickly and becomes an acidic hydrothermal fluid. It is also conceivable that chlorophaeite decomposes due to the formation of acidic gases and primarily, of hydrogen chloride. Under surface conditions these chemicals act as highly effective solvents in basalt melts [6]. The concentration of these gases in lavas that poured over the sea-floor, being under relatively high pressures should be higher than in continental lavas. Acidic gases in the cooling melt that are in contact with water may form acids of low concentrations. This leads to chlorophaeite decomposition, while the other rock components remain unaffected.

Available data do not yet assign preference to either of the two suggested acidic leaching processes by which chlorophaeite is effected. Both may influence the development of the acidic medium in the cooling oceanic lavas.

Diffusional-capillary flows should form in each portion of the cooling lava, bounded by fracture contacts. The quickly warming, acidified sea water that enters apparently dissolves the Mg—Fe glass (chlorophaeite). After destroying the soluble components, the fluid reaches the surface through contraction fractures. One would expect precipitation of the substance at this geochemical barrier; the location where the solutions meet relatively cool, oxygen-rich sea water of near-neutral pH values. Part of these substances precipitate in rock zones immediately adjacent to fractures; another portions settles within the fractures and form veins. The remainder enter the sea water.

How does this model apply to young basalts, slightly altered by subsequent processes? Studied samples include those, taken from the Tadzbur Rift (Gulf of Aden), sampled by POA "Paisis" (under the supervision of Yu. A. Bogdanov) during the 9th Cruise of r/v Academician M. Keldysh. The rocks were porphyritic olivine basalts. The olivine crystals essentially were fresh. The rocks were highly crystallized, with an intersertal-ophitic groundmass, including subsequential amounts of clinopyroxene and basic plagioclase crystals of elongated-tabular shape. Light-brown glass occurred in the basalt groundmass, usually filled with inclusions of ore minerals and unidentified microlites. The refraction index was significantly lower than that of Canada balsam, indicating acidic composition. The basalts were highly porous (15–20 volume percent) and the void diameter ranged between 0.1–3 mm. Large, rounded degassing voids occurred. Most of the pores were xenomorphic; their morphology determined by the intersecting pyroxene and plagioclase microlites that intruded into the voids (Fig. 1e).

Based on these facts, the authors interpret the data as indicative of a secondary origin of the voids, due to leaching.

8–10-mm-wide dark halo zones were observed inside the samples. They were parallel with all the structural surfaces and occurred along fractures. The pores in these zones are partially or completely filled with secondary products of golden yellow or green and red coloration. The latter ones occur mostly in spaces, located closer to structural surfaces or fractures. These substances had been separated and identified by a complex of physical and chemical methods: x-ray studies, Mössbauer spectrometry, infrared spectroscopy and others.* Based on these studies and chemical analysis data by the use of microprobe (Table 3), it has been concluded that the newly formed green and yellow substances are composed of glauconite crystals (c.35%), dioctahedral Al-smectite (c.25%) and trioctahedral glauconite (c. 40%). These substances are poorly crystallized. The newly formed reddish substances in this phase contain iron hydroxide admixtures. The presence of trioctahedral oxismectite in the reworked substances within the dark halo zone and the chemical composition of the phase does not contradict the previously discussed model. Based on this composition, these substances may have formed completely as the result of the dissolution of chlorophaeite and its subsequent precipitation at the geochemical barrier. As earlier noted, similar high-K glauconite-smectite products within the dark halo zone have been described by a number of authors [17, 19].

Due to large-scale hydrothermal processes, secondary mineral formation involved greater complexities in basalts, explored by drillholes along the rift flank zones. The study of late hydrothermal basalt alteration was not our task. We only note that in relatively old basalts, subjected to hydrothermal solutions, the leached interstitial voids became filled by various secondary minerals; primarily by high-Mg saponites. Second-generation glauconitic-celadonic clay minerals may also form.

*Results of these studies will be discussed in greater detail in a forthcoming paper.

The most important conclusion stems from the theory of initial leaching of Mg—Fe glass (chlorophaeite) from basalts. This would account best for the loss of great volumes of substances to sea water and their subsequent settling as components of pelagic sediments. The great importance of this process quantitatively is based on the universal presence of interstitial clay mineral formations or secondary pores in place of femic glass (chlorophaeite) in oceanic crystalline basalts. These components represent 2-10% of the rock volume.

PETROGENIC AND TRACE ELEMENTS IN CHLOROPHAEITE

We present an interesting tabulation of the petrogenic and trace elements that may have been leached out during dissolution of Mg—Fe glass (chlorophaeite).

Table 1 gives analysis results of chlorophaeite from continental and oceanic basalts. Among the petrogenic components, ores are represented only by iron. The Mn content is lower than in the corresponding basalts. Decomposition products of femic glass have a composition that may have served as source material for the formation of nontronitic or glauconitic-celadonitic dioctahedral layer silicates.

Information received from the study of Devonian continental basalts of the Timan may be used in the preliminary evaluation of ore minerals in Mg—Fe glasses and oceanic basalts; their petrogenic composition is similar. No study has yet been made on the trace element composition of chlorophaeite of oceanic basalts; the samples, taken from Drillhole 304 DSDP and available to us are of small volume and low chlorophaeite content.

The trace elements occur in the monomineralic fractions, separated from ten Timan basalt samples. Analyses were performed on quartered bulk samples that allowed comparison of the trace element content in chlorophaeite and in basalt as a whole, between pairs of samples. Quantitative spectral analysis results by L. S. Sukneva and M. V. Odintsova (Geological Institute, Yakut Branch, Siberian Department, Academy of Sciences of the USSR) are given in Table 4. The distribution coefficient (K_d) was calculated for each element in the basalt-chlorophaeite pairs. The following formula was used: $K_d = C_x/S_b$ with $K_d > 1$; and $-K_d = C_b/C_x$, with $K < 1$, with S_x = content of given in chlorophaeite and S_b = same, in basalt. Analysis of the data presented (Fig. 2) shows that the K_d values, as a rule, are either positive or negative. Such a statistically consistent element distribution relationship between chlorophaeite and rock indicates existence of an orderly pattern.

Chlorophaeite had been enriched in a number of ore elements (Sn, Pb, Cu, Ni, and Co) in comparison with corresponding basalt samples. A significant enrichment in Rb, Ba, Zr, B, and other elements that accumulated in magma residue also took place during basalt crystallization. Elements (Sr, Zn, Cr, V, Ge, and Sc) that isomorphously entered magma mineral lattice structures, on the other hand were scarcer in chlorophaeite than in basalt.

EXPERIMENTAL STUDY OF Mg—Fe GLASS (CHLOROPHAEITE) LEACHING

The conditions that prevailed during chlorophaeite leaching in sea water were recreated for the experiment, including also the initial concentrations of petrogenic and trace elements that may be extracted from the rocks during this process and participate in sediment formation.

Results of the experiments were strictly of preliminary nature and also indicate a general trend of the process. They have been conducted on Timan basalts. Currently, we do not possess sufficient amounts of chlorophaeite, isolated from oceanic basalts.

Experiments with Small Basalt Samples. Small (3-5 mm) basalt fragments (sample #18-83) that contained chlorophaeite were scalded with sea water in a platinum vial at 400°C temperature and 500 bar pressure for 18 h. This experiment was performed by I. V. Kholodkovich at the Far Eastern Mining Engineering Institute, Far Eastern Branch, Academy of Sciences of the USSR. Binocular microscope study of the samples after the experiment indicated formation of a friable, porous iron oxide matter that replaced chlorophaeite. Complete leaching thus did not take place, although chlorophaeite was totally eliminated. The experiment took place in a closed system, with an acidic (pH = c.2.5) medium reaching a temperature of only c.350°C. During cooling of the vial, the pH value of the sea water was reduced and the iron oxides apparently were resettled in the newly formed voids. Locally, along with the friable iron oxides strongly oxidizes (red) chlorophaeite has also been identified in the thin section. Results of chemical analyses of this altered chlorophaeite (Table 5) indicated a significant composition change; loss of Al_2O_3 and SiO_2 and the addition of FeO. In the second series of experiments the natural heating of sea water to c.350°C was imitated by adding a few droplets of HCl in 100 ml of sea water* that created a pH value of c.5. The samples were boiled for 30 h. The thin section obser-

*The Lyman—Fleming formula for synthetic standard sea water was borrowed from [1].

vations indicated partial destruction of chlorophaeite under these conditions, resulting in color loss and a friable consistency. A total loss of the matter with formation of interstitial voids, similar to those described (Fig. 1e), occurs only when added HCl results in a pH value of c.1.

In none of the observed instances has the alteration of minerals of magnetic origin and of the basalt groundmass been observed. Only partial oxidation of Ti-magnetite was possible.

Experiments with Precipitated Chlorophaeite fraction (5-50 μm grain size, c. 1 g specimens). The samples were boiled in standard sea water for 30 h and a c.5 pH value was maintained through addition of HCl. Index liquids indicated that the residual product was strongly decomposed (bleached and corroded) chlorophaeite. The solution became pale green, was decanted and neutralized, with the addition of NaOH that resulted in a pH value of c.7.4-7.6. A friable, green substance precipitated in this process. Within one day the substance became stratified into a lower greenish-blue and an upper yellow layer. In a week it turned yellowish brown.

The sediment was separated from the solution and the salt rinsed off with distilled water. The chemical (microprobe) sediment analysis of three chlorophaeite samples indicated their significant Al_2O_3 , SiO_2 , and FeO content (the main petrogenic components of pelagic deposits; Table 5). In addition, the sediment displayed a very high MgO and low total-oxide content. This was due to hydrotalcite formation in the sediment from elements that had been leached out of chlorophaeite and accumulated in sea water (Mg and anions). X-ray powder diffraction analysis of the sediments included broad 7.72-7.80 and 3.84-3.80 Å reflections, produced by an apparently poorly crystallized hydrotalcite phase.

Table 6 displays the trace element content in the synthetic sediments, chlorophaeites and corresponding basalt samples. Analysis of data, shown in Table 7, indicates that despite the significant "dilution effect" of the leached matter with regard to Mg and SO_4^{2-} and CO_3^{2-} anions due to loss from sea water, the concentration values of many elements (B, Zr, Sn, Pb, Zn, Ni, Co, and Sc) in the sediment were markedly higher than in chlorophaeite, and, correspondingly, in basalt.

The data were compared with concentration values of these elements in metal-bearing and pelagic sediments. The analysis of the data (Table 7) indicate that, in general, the trace element concentrations are at the level of pelagic sediments but markedly smaller than in metal-bearing sediments. Mn is an exception; its concentration was markedly higher in synthetic sediments than in pelagic clays.

These experiments indicated that the quantitative and qualitative composition values of petrogenic and trace elements, extracted during chlorophaeite leaching, approximate the composition of regular pelagic clays. The effect of initial basalt alteration on ore concentrate formation in sediments is hard to establish. Apparently, the mobilized matter does influence the background concentrations of the authigenic sediment fraction.

Thus, while admitting the importance of introduced new substances during desintegration of large-scale hydrothermal systems and of underwater weathering of basalts and hyaloclastic matter, the present authors would also encourage consideration and study of the impact by initial basalt alteration on oceanic sediment genesis. A conclusive solution of the problem apparently is feasible through direct, systematic studies of oceanic basalt eruptions.

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SEDIMENTATION FEATURES IN THE MIDDLE MIOCENE PRE-CAUCASUS BASIN IN CONNECTION WITH PALEO-DON ACTIVITY

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The lithologic-facies features of the western, central, and eastern parts of the middle Miocene Precaucasus paleobasin and their connection with the configurations of the Miocene river network are considered in this article. A conclusion is drawn on the migration of the mouth of Russian platform's largest river, the paleo-Don, during the middle Miocene.

Miocene time, and middle Miocene time in particular, is one of the most interesting periods in the history of the Precaucasus basin. Right in middle Miocene time, the place of the extensive Maikopsk sea with its rather homogeneous sedimentation features was taken by a basin with a smaller area, but significantly greater differentiation in the conditions of sediment accumulation.

Operations were conducted over a period of years in the sedimentary rock geochemistry laboratory of the Geological Institute of the USSR Academy of Science, under the guidance of V. N. Kholodov. These efforts were devoted to lithologic-facies and lithologic-geochemical study of middle Miocene deposits of the Precaucasus. Apparent in their results was a lithologic-facies profile, extending more than 1000 km along the Caucasus range from a section at the Sulak river on the east to a section at the natural boundary Malyi Kamyshtak on the west. The profile includes 16 precisely described and tested sections, the total thickness of which comes to approximately 7 km. Territorially, the profile is broken into three parts: western, central, and eastern, corresponding to the western, central, and eastern zones of the paleo-sea, which are distinguished by their sedimentation conditions. The western zone includes the Kerchenskii peninsulas and the Western Precaucasus, while the central and eastern zones correspond to the Central and Eastern Precaucasus.

The eastern and western zones correspond in tectonic plan to the Tersko-Kumsk and Azov-Kubansk depressions and the forward depressions which complicate them, and the central zone corresponds to the Stavropol'sk anticline and Belomechetsk downwarp which separate the depressions.

Taking advantage of the results of studying this profile [17, 21, 22], as well as literature data [1, 2, 6-8, 10, 11, 15, 20, 23, and others], this article will briefly characterize the features of middle Miocene deposits in the different zones of the paleobasin.

The western zone (Fig. 1). Deposits of the middle Miocene pre-Black sea and Crimea are represented by various shallow water sea facies. Deposits of lime-clay sediment facies of relatively deep water parts of the sea appear only in the Western Precaucasus in the axial part of the paleobasin. The fraction of sand deposits in the section is minimal in the western zone of the middle Miocene basin. They are mainly developed in the northern part of the Western Precaucasus, and are represented by deposits of interlayered sand-silt clay sediments from the still shallow water facies, as well as by silt-sand sediments from the moving and strongly moving shallow water facies, including the near-mouth facies. It is necessary to note that the distribution area of these sand deposits is noticeably increased at the end of Karaganian and Konkian time, while the facies contours in plan view (see Fig. 1b, c) suggest the existence of paleo-rivers which occupy the place of the contemporary Don. It is necessary to say that the presence of a rather large river which flowed into the western part of the paleo-sea in the region of the contemporary Don mouth in Karaganian-Konkian time is confirmed by findings in the Don floodplain at Melikhovskii station and at several other places of buried valleylike ravines with steep slopes, 500 m and more wide, and up to 60 m deep. The valleys were produced in deposits of the Khar'kovsk suite of Paleogene and pre-Paleogene sand-clay deposits, among which dark clays crowded by plant remnants were widely dispersed. These deposits acquired the designation the Melikhovsk suite [19]. Analysis

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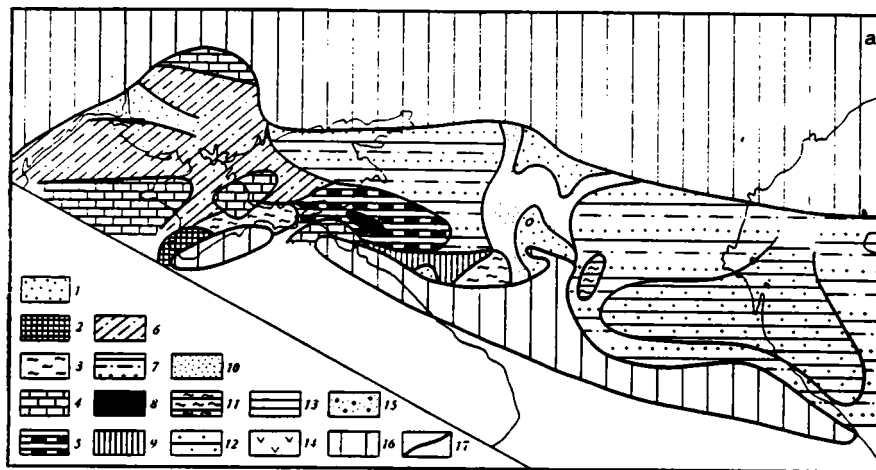
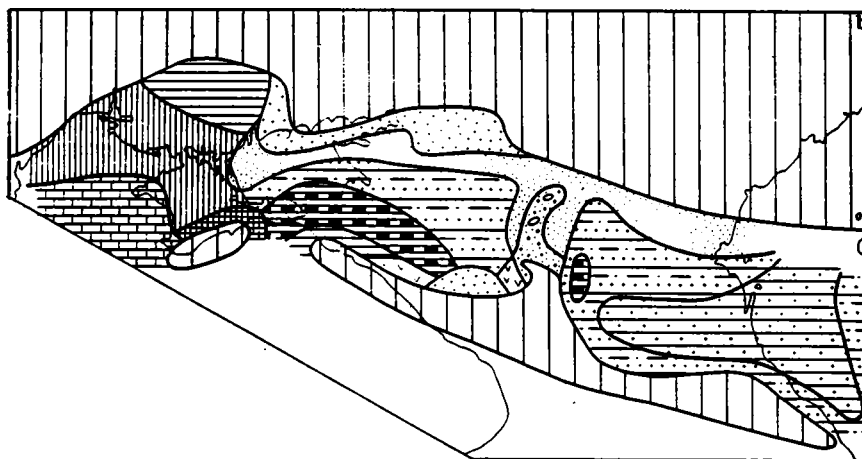


Fig. 1a, b



of spore-pollen complexes from flora-bearing sequences of the Melikhovsk ravines carried out by E. N. Ananova, made it possible to attribute them to the Karaganian-Konkian. In addition, shells of *Spaniodontella pulchella* Baily were discovered in these same deposits at Bogaevsk station, while ostracods characteristic of the Karaganian were found in downstream reaches of the Sal river. These data made it possible for G. N. Rodzyanko to draw a conclusion on agreement of the position in plan of the valleys of the Miocene and contemporary Don [19] (Fig. 2a).

A group of silty-sand sediments from a strongly moving shallow water facies, including the near-mouth part, is recorded in Chokrakian deposits of the northwest part of the western zone. These deposits apparently mark the mouth of the paleo-Dnieper. In the middle Miocene the water and solid runoffs of this river were relatively small. This is indicated by the small thickness and distribution area of the clay-sand sediments which accumulated during Chokrakian-Karaganian time in the mouth region, and also by the absence of the notable ravines of the paleo-Don. They do not exceed 20-30 m in basin of lower Dnieper [16].

Central Zone. This part of the basin represents an intermediate, transitional zone between the western and eastern basins of the middle Miocene sea. Here, in the limits of the Stavropol'sk arch, was accumulated a relatively thin sequence in comparison with the western and eastern zones, of clay-sand deposits from the facies of silt-sand sediments of moving and strongly moving shallow water, including near-mouth deposits (see Fig. 1a-c). The deposits bear the signs of multiple erosions. Wavy and cross bedding are often observed in the sandstones, and they often acquire oolitic structure due to carbonate "coatings" put onto quartz sands. This all attests to the shallow water character of sediment accumulation and to the repeated rewashing and redeposition of terrigenous material.

In the Belomechetsk downwarp, in distinction from the Stavropol'sk arch, mainly clay, silty-clay and carbonate-clay deposits accumulated in the middle Miocene. Practically all of the sand material was concentrated in the lower part of the Chokrakian deposits in the form of thick sand interlayers. On the Stavropol'sk arch the general predominance of the sand material fraction in the section decreases from the bottom upwards. The platformal origin of the sand deposits is confirmed by study of terrigenous mineral complexes, which showed a wide distribution in the sand sediments of a group of stable minerals, such as zircon, rutile, tourmaline, garnet, as well as the constant presence of kyanite and

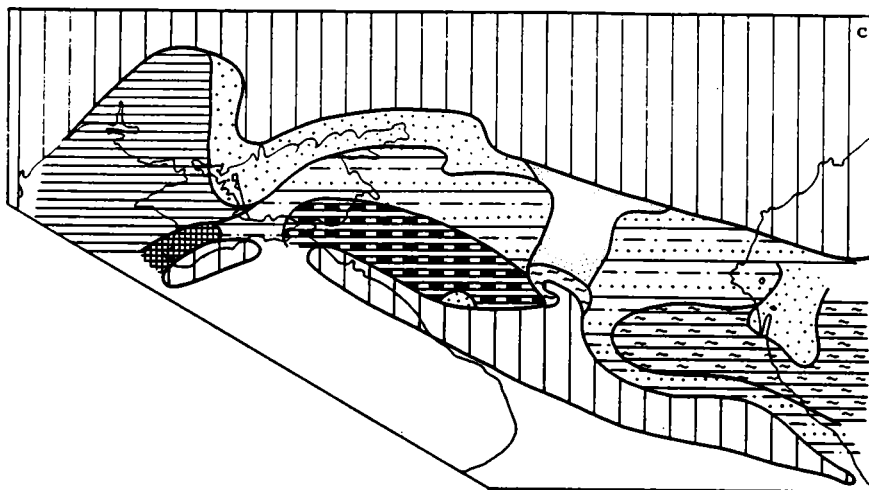


Fig. 1. Lithologic-facies scheme of Chokrakian (a), Karaganian (b), and Konkian (c) deposits of the Precaucasus (from data in [1, 2, 10, 15, 20, and 23] with additions by the author). 1)-15) are depositional facies: 1) silty sand sediments of strongly moving shallow water, including near-mouth shallow water (MMD); 2) sand—carbonate sediments from the near-shore zone of moving shallow water (MPK); 3) sand—carbonate—clay sediments from near-shore shallow water (MPT_κ); 4) clay—carbonate sediments of slowly moving shallow water (MMI); 5) lime-clay sediments from a relatively deep water part of the sea (MGK); 6) clay—silty sand sediments from a shallow water part of the sea (MMK); 7) interlayered sand—silty clay sediments from slowly moving shallow water (MMM); 8) silty sand sediments from an underwater uplift (MMP_ρ); 9) carbonate—clay sediments from near-shore shallow water (MPI); 10) silty sand sediments from moving shallow water (MMP); 11) silty clay sediments from a relatively deep water part of the sea (MGT); 12) sand sediments from bottom currents and silty clay sediments from relatively deepwater parts of the sea (MGP, MGT); 13) clay sediments from stagnant near-shore shallow water (MPZ); 14) silty clay sediments from near-shore shallow water (MPT); 15) silty sand sediments from strongly moving shallow water (MMB); 16) dry land; 17) boundary facies.

staurokite. A similar complex of terrigenous minerals definitely indicated the Russian platform as the source of material for the sand interlayers [3, 4, 9, 12]. It is interesting to note the fact that V. A. Grossgeim [12] concluded that sand material entered the basin in two places: in Stavropol' and in the Northern Caspian region (Fig. 3) based on analysis of the scheme of the terrigenous—mineralogical provinces of Chokrakian deposits.

Apparently, in early Chokrakian time, in the basin's central zone, a coarse sand material fraction entered from the platform, and the sand supply was subsequently sharply constricted. The high sand content of the entire middle Miocene section on the Stavropol'sk arch is explained by a tendency towards uplift of this structure in Chokrakian—Karaganian time, as a result of which the sands accumulating in early Chokrakian time were repeatedly reworked and redeposited in conditions of shallow water, whereas formation of the clay sequence occurred in the subsiding Belomechetsk downwarp.

Sand material in the early Chokrakian deposits was supplied by large platformal rivers whose activity began to be reflected in the thicknesses of deposits accumulating in the northern part of Stavropol'ya. If data from the Atlas of Lithologic—Paleogeographic Maps is employed [2] to construct contours of Chokrakian thicknesses, then, disregarding the multiple rewashings which significantly distorted the initial sediment distribution map on the Stavropol'sk arch, it is nevertheless possible to speak with certainty of the existence of a large river in the northern part of the region, the output cone of which is reflected in the isopach drawing (Fig. 4). It is necessary to note that traces of the paleoriver are no longer noted on the map of Karaganian deposits.

It is clearly apparent on the Chokrakian equal thickness scheme that the output cone of the platformal river is distributed over the continuation of a narrow winding canyon, which is incised almost 400 m into Maikopsk deposits and occupied by ingressive-marine deposits of Chokrakian age (from spore-pollen analysis data). This canyon, which was investigated by N. I. Luparev and then studied by V. S. Kosarev [13, 14] in the region of Divna station, lies on the

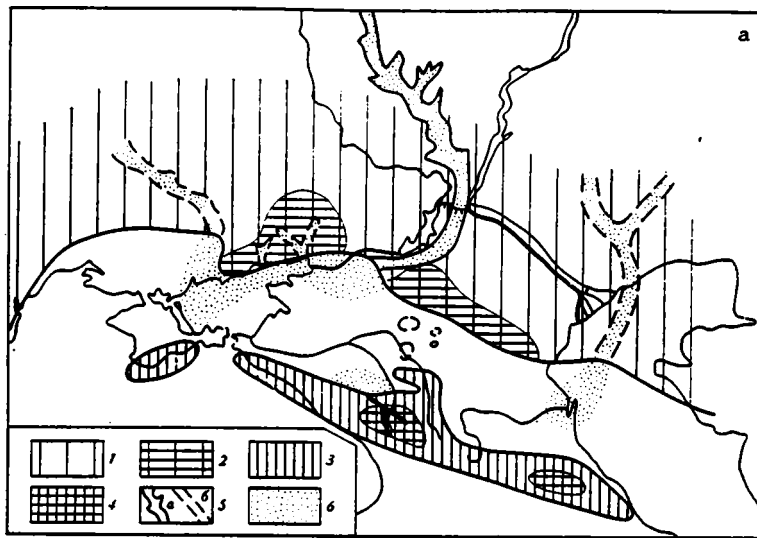
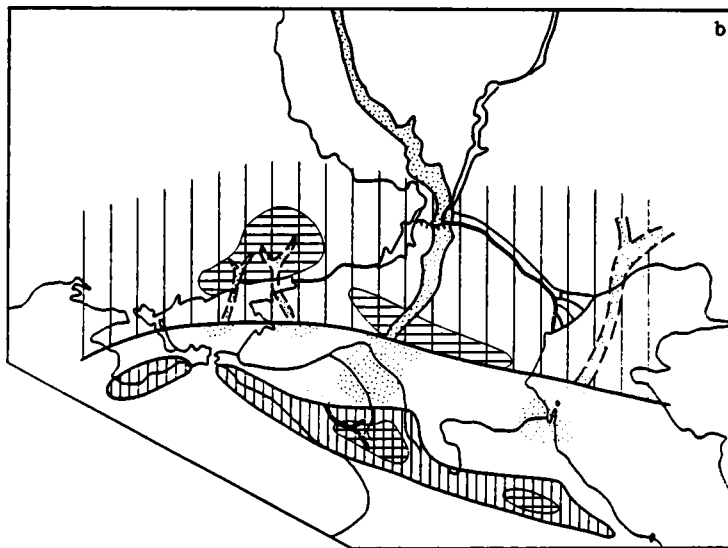


Fig. 2a, b



continuation of the paleo-Don which is traced over more than 1000 km, and in the opinion of Yu. I. Iosifova [16], itself represents the mouth portion (see Fig. 2b).

Eastern Zone. Alternation of thick silt-clay and sand packets in the section is a characteristic feature of this part of the middle Miocene paleobasin. Clay deposits belong mainly to the silt-clay sediments of relatively deep water facies, distant from the coastal part of the epicontinental basin. The majority of the sand interlayers are completed by deposits of sand sediment facies of Don genesis, originating from the continuation of river flow into the marine basin. Some textural-structural features of the sandstones are convincing on the similar origin of the sand interlayers. As a rule, the lower contact of the sand interlayers is sharp and contains small pebbles of quartz and marls, and sometimes rather coarse (up to 20 cm in diameter) fragments of clay and clay balls. The lower, sometimes rather thick part of the sandstones are generally rather homogeneous in composition and made up of relatively pure fine and medium grained (sometimes coarse grained) quartz sand, while the particle size decreases towards the top. Higher in the sandstones are apparent interlayers of siltstones and clays, whose quantity increases upwards. The absence of faunal remnants and the presence of oblique monodirectional flow layering is characteristic of the sandstones. Measurements of slope angles in the crossbeds enabled N. B. Vassoevich and V. A. Grossgeim [8] to construct paleoflow maps for the middle Miocene paleobasin, and thereby to define more accurately the position of the mouth of the paleoriver which was supplying sand material to the Eastern Precaucasus. In agreement with their constructions, the mouth of the paleoriver was positioned in the region of the contemporary North Caspian. Such a picture of the paleomouth also confirms the scheme of terrigenous-mineralogical provinces in Chokrakian deposits (see Fig. 3), where the very form of the terrigenous-mineralogical provinces in plan clearly reflects two sources for terrigenous material: one in Stavropol' and

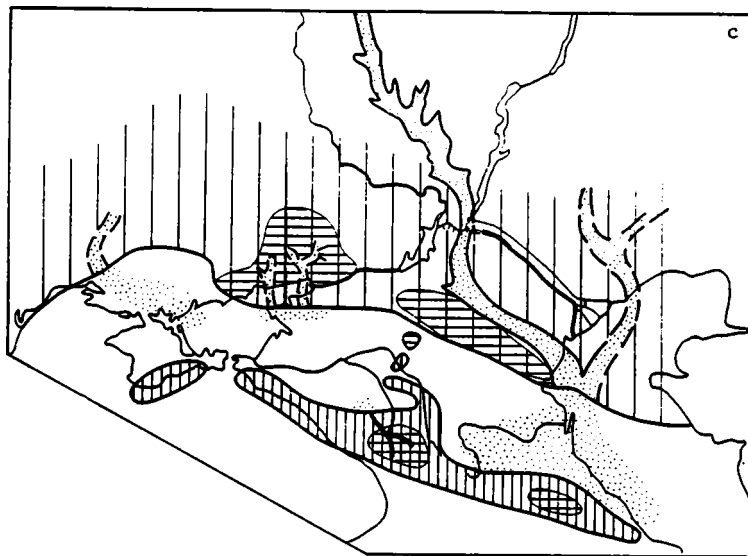


Fig. 2. Paleogeographic scheme of the Precaucasus for middle Miocene time (a) Karaganian-Konkian; b) early Chokrakian; c) Chokrakian-Karaganian): 1) northern dry land; 2) elevated parts of northern dry land; 3) Caucasus dry land; 4) elevated parts of Caucasus dry land; 5) contours of paleoriver valleys (a) traced; b) proposed); 6) areas of predominately sand material accumulation.

another in the region of the Northern Caspian. In addition, the very complex of terrigenous minerals, in which kyanite and staurolite play a significant role, irrefutably indicates a platformal source of sand material.

River valley remnants in immediate proximity to the proposed mouth of the paleo-river are almost undetected, however findings of Yashkul'sk Suite deposits which are represented by shallow water continental—marine sand—clay sediments with interlayers of coarse grained cross-bedded sands of river type [5, 18], enabled V. A. Brylev [15] to reconstruct the position of the paleo-Don valley and to direct its lower flow towards east into the side of the Caspian Sea (see Fig. 2c). Deposits of the Yashkul'sk Suite fill wide and deep valleys which are developed in rocks of the Maikopsk Suite and are oriented from west to east. The amplitude of the buried relief reaches 200 m. Widening and deepening in the eastern direction, it is as if they flow into the pre-Caspian lowland. The middle Miocene age of the Yashkul'sk Suite is established on the basis of findings of Chokrakian fauna *Leda fragilis* Chemn., *Spiralis* sp, as well as of a complex of spores and pollens characteristic of the Chokrakian-Karaganian.

For a correct understanding of the features of sediment accumulation in the eastern zone of the paleo-sea, it is necessary to note that sand interlayers are widely distributed only beginning in the middle part of the Chokrakian. Essentially clay deposits were accumulated over a large part of the territory of the Eastern Precaucasus in early Chokrakian time. Only in northern Dagestan are sand sediments known from the very base of the Chokrakian. The nonrandomness of this phenomenon is also confirmed by some variations in the terrigenous mineral complexes of the lower, essentially clay, and upper, sand—clay, portions of the Chokrakian deposits, which apparently indicate changes in the source of the terrigenous material washing into the terrigenous material washing into the basin [11].

Thus, examination of the lithologic-facies characteristics of the Precaucasus Chokrakian—Karaganian paleobasin, as well as analysis of the distribution of the paleo-ravines of middle Miocene river valleys, carried out by the efforts of a series of investigators [5, 16, 19], leads to a paradoxical situation: in each of the three zones of the paleobasin significant masses of terrigenous material are carried out of the same river — the paleo-Don. Different authors have similar pictures of a large part of this river's paleo-valley, and variant readings are apparent only in its lower course. It is certain that the paleo-Don left traces of its activity in the Western, Central, and Eastern Precaucasus, but, and it is necessary to stress this, these traces are *noncontemporaneous* and arose as a result of the fact that this river twice changed the direction of its lower course during the middle Miocene.

In fact, the accumulation of the basic mass of sand sediments in the central zone of the paleobasin occurred only in the early Chokrakian, and ingressive deposits in the Stavropol'sk canyon are dated as Chokrakian. In the eastern zone, interlayers of quartz sandstones were accumulated during Chokrakian and Karaganian time, excluding early

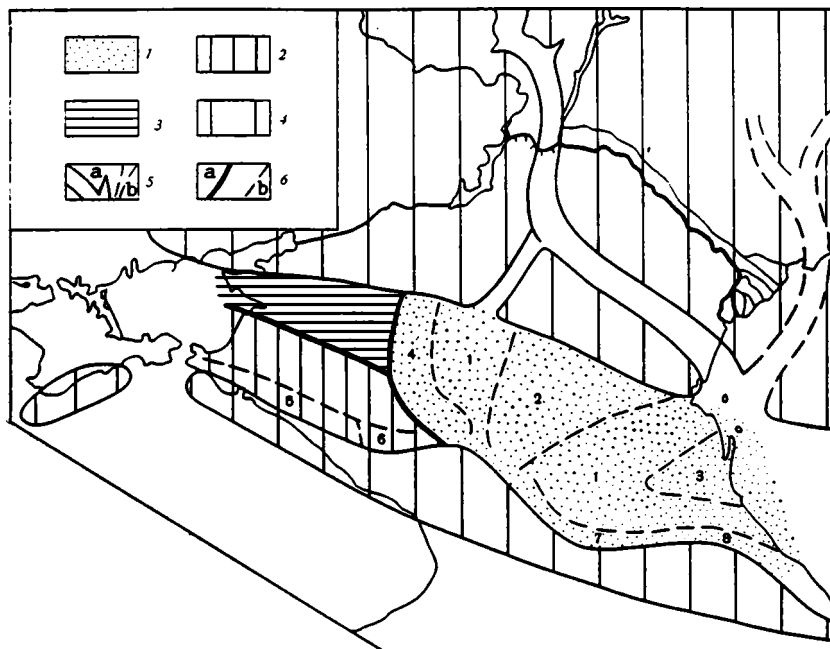


Fig. 3. Scheme of terrigenous-mineralogical provinces of Chokrakian deposits (after V. A. Grossgeim [12]): 1)-3) provinces: 1) Eastern Precaucasus, 2) Kubansk, 3) Don; 4) dry land; 5) contours of paleoriver valleys (a) provinces; b) subprovinces). The numbers on the scheme signify subprovinces: 1) Sunzhensk; 2) Ozek-Suatsk; 3) Makhachkalinski; 4) Cherkessk; 5) Western Kubansk; 6) Eastern Kubansk; 7) Nal'chiksk; 8) Daradinsk.

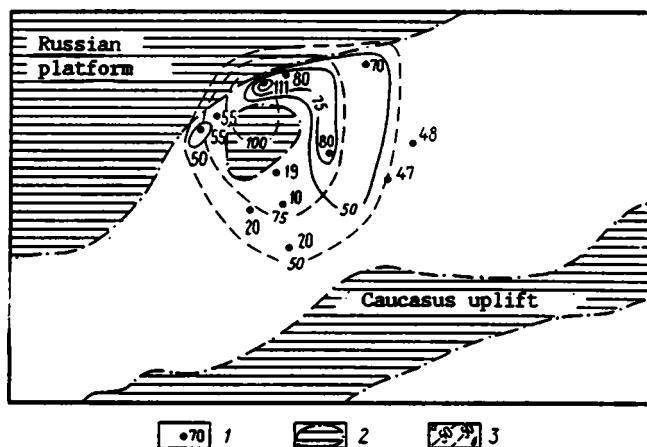


Fig. 4. Isopachs of Chokrakian deposits of the northern part of the Stavropol'sk arch. 1) well and thickness of Chokrakian deposits discovered by it, after [2]; 2) zone of complete erosion of Chokrakian deposits; 3) isopachs of Chokrakian deposits (a) from well data; b) assumed).

Chokrakian and late Karaganian, and deposits of the Yashkul'sk Suite are dated as Chokrakian and Karaganian. Finally, in the western zone, the fraction of sand deposits is increased at the end of the Karaganian-Konkian, and deposits of the Melikhovsk Suite are dated at this time.

As the large paleo-Don river artery was formed in pre-middle Miocene time, the huge size (the total length of the valley exceeded 1200 km, the width in the middle part was 40-50 km, the drainage area reached approximately $1.5 \cdot 10^6 \text{ km}^2$), the linearity of the outlines, and the duration of the valley's existence indicates the significant role of tectonics in formation of this river. Tectonic activity and transgressive-regressive motions of the paleo-sea also apparently determined the changes in the direction of the course of the paleo-Don was positioned in the northern part

of Stavropol'. As a result of sea regression and deepening of the erosional base, which was evidently connected with the process of alpine tectogenesis acting on the Precaucasus territory in the middle Miocene, the paleo-Don in short time carried significant masses of sand material out to the Stavropol'sk arch and into the Belomechetsk downwarp, and at the same time cut a deep 400-m canyon in the Maikopsk deposits developed in the coastal zone. In the eastern part of the sea, sand sediments were only input into the Northern Dagestan region, and the paleo-Volga evidently served as their supplier. It is difficult to say anything definite about the activity of the paleo-Volga, since remnants of its Miocene valley were either subsequently annihilated or are have not yet been found [5]. During subsequent transgression of the sea, rising of the Southern-Ergeninsk and Donetsk uplifts created an obstruction to the paleoriver's path, and at the time of subsequent regression of sea the paleo-Don was constrained to turn to the east and form a valley in the Yashkul' region, and to form a mouth in the northern part of the contemporary Caspian Sea close to or combined with the paleo-Volga. The combined activity of these two large platformed rivers led to the formation of thick sand interlayers over a greater part of the area of the eastern zone. Successively then, a series of transgressive—regressive motions of the sea led on one hand to the formation of roughly 20 sand interlayers in the Chokrakian-Karaganian sequence of the Eastern Precaucasus, and on the other hand to the formation of a complete series of rather deep (up to 200 m) paleo-ravines filled by deposits of the Yashkul'sk suite and deepening towards the side of the Caspian Sea. Finally, somewhere in the second half of the Karaganian, after one of the transgressions, the paleo-Don once again changed the direction of its lower course, turning to the west. However the intensity of tectonic motions, judging by the depth of the paleo-ravines, over the length of the middle Miocene gradually declined, and at the end of the Karaganian-Konkian it was not great, owing to the fact that the influence of the paleo-Don the lithologic-facies picture of the western zone of the basin was small, and the ravine of its paleo valley, filled by deposits of the Melikhovsk Suite, did not exceed 60 m.

Thus, the paleo-Don, the largest river artery of the Russian platform in middle Miocene, had a huge influence on the processes of sediment accumulation in the Precaucasus paleobasin. The migration of the paleo-Don mouth during middle Miocene time to a significant degree caused the lithologic-facies features of the western, central, and eastern zones of the paleo-sea.

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ORIGINS OF ORDOVICIAN OIL SHALE IN THE BALTIC SYNECLISE. PAPER I:

DICTYONEMIC SHALES

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Dictyonemic shales of the Baltic region are shown to be formations of the sublittoral facies of the sea basin. The main producers of their organic matter were benthic microbial organisms living in calm desalinized waters enriched in allochthonic humic acids. The limited destruction of organic matter during diagenesis is explained by its rapid conservation in lithified sheaths of microorganisms and acidulation of the environment.

Ordovician dictyonemic shales and kukersites in the Baltic region occupy a peculiar place among platformal Lower Paleozoic carbonic rocks. Besides being of practical value, these rocks are interesting because they exhibit highly individualized features reflecting the diverse conditions of their accumulation.

The genesis of dictyonemic shales and kukersites has long attracted the interest of investigators, but difficulties in establishing the source of organic matter often made answers impossible or debatable. At the present time, there are no reliable explanations for certain features of their composition.

In the past few years, cooperation with microbiologists (V. M. Gorlenko) shed new light on the origin of oil shales in the Baltic region and helped bring into a system disparate data of various investigators.

Stratigraphically, dictyonemic shales are associated with Pakert horizon of the Lower Ordovician, represented exclusively by terrigenous sediments. The lower half of the bed (up to 10 m) consists of inequigranular quartz sand with typical wavy oblique lamination of shallow-sea marine sediments, numerous minor erosions, and phosphatized mollusk shells. The top part (0.1-8 m) is a consistent monotone member of dictyonemic shales traceable along the entire southern slope of the Baltic Shield. This uniformity is violated only in areas where the member is replaced by sands. Their light silicic interlayers appear in dictyonemic shales; these are thin layers (up to 3-4 cm) consisting of sponge spicules, grayish silt thin layers, and pyrite and anthraconite lenses.

Lithologically, the shales are a fine-laminated silty-pelitic dark-gray rock with a largely uniform content of organic matter (8-12%). Amino acids and humic acids have been found in the organic component besides kerogen.

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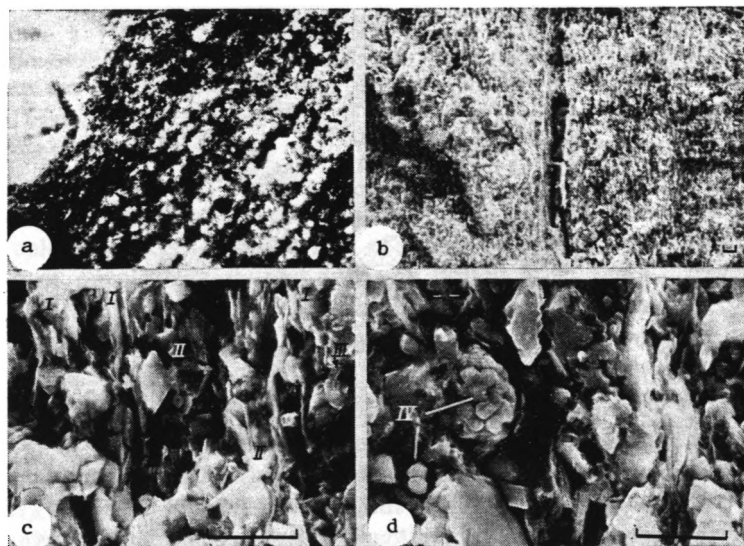


Fig. 1. Lithified remains of microorganisms (producers of autochthonic organic matter) of dictyonemic Ordovician shales in the Baltic region: a) separated threadlike cyanobacterium (polished section in optical microscope with a dark field condenser (magn. $\times 430$); b-d) microstromatolitic laminated texture of a mat (carbon-powdered shale, broken surfaces under a scanning electron microscope, bar $10\ \mu\text{m}$). I) Common sheaths of *Microcoleus chthonoplastes* microcolonies; II) sheaths of individual threads; III) sheaths of *Chloroflexus* green bacterium; IV) framboidal pyrite after a colony of sulfobacteria.

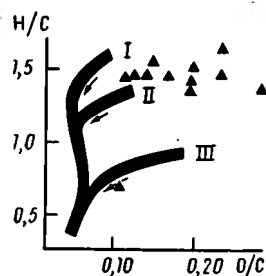


Fig. 2

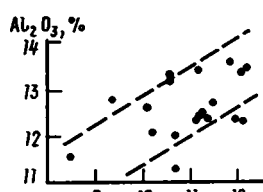


Fig. 3

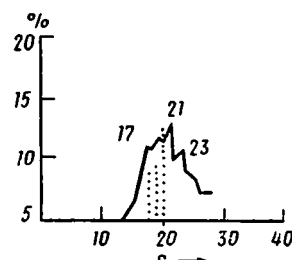


Fig. 4

Fig. 2. Position of figurative points of dictyonemic shales according to kerogen classification diagram [35]. Arrows show the direction of geochemical evolution: I-III) kerogen types (I — algal; II — mixed; III — terrigenous). Based on data reported in [13, 14].

Fig. 3. Ratio of C_{org} and Al_2O_3 contents. Based on data reported in [13, 14].

Fig. 4. Distribution of normal and isoprenoid alkanes in oils of CBA fraction.

Generally, the contents of these components rise westward toward increased homogeneity of the shale member section [9, 18, 21].

The kerogen of dictyonemic shales according to its petrographic investigation [6, 23] consists mainly of amorphous organic matter (saprokollinite),* finely mixed with a clayey matter. Structural fragments (algenitohallomite) are of a subordinate importance; the same is true of pseudovitrinite and cutinite. Coaly detritus and humic gelled inclusions are observed in polished sections [13]. A study of the chemical composition of kerogen [11, 12] showed a

*The microcomponent composition of shale kerogen is described here according to the classification of Bogolyubova, Timofeev, and Pronina [3].

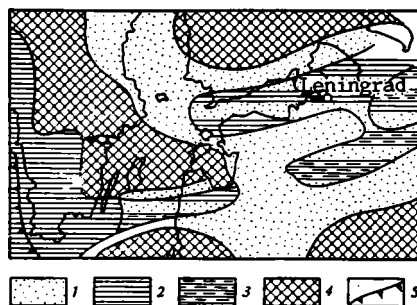


Fig. 5. Lithologic-paleogeographic map of the northwestern East European platform during the principal dictyonemic shale accumulation period (after [19], with additional data): 1) littoral sediments (quartzose inequigranular sands with oblique wavy lamination and signs of interruption); 2) sublittoral sediments (dark-gray graptolitic ooze); 3) shallow-sea marine sediments (gray clays); 4) land; 5) platform boundary (Tornquist line).

relatively small variation of carbon content (63.6–75.4%) and oxygen content (10.7–24.2%), a low hydrogen content (7.7–9.0%), and a high nitrogen level (up to 4%).

Chloroform bitumoid (CBA) of dictyonemic shale [1] has virtually no properties in common with petroleum matter. All of its components are depleted of hydrocarbon structures; it has a high content of oxygen groups, mainly of phthalatic type in benzene and alcohol benzene resins. In oils, the *n*-alkane series ends at C_{28} ; the isoprenoid series ends at C_{20} . Liquid *n*-alkanes amount to just 5% of the total quantity; in the isoprenoid series they are absent.

The mineral composition of dictyonemic shales [2, 10, 13, 22] is determined by pelitic particles (up to 50–70%) and minerals of the silt fraction (up to 30% and more). The clay fraction consists of montmorillonite, hydromica, swelling hydromica, and muscovite. Kaolinite and chlorite are also present. The silt fraction consists almost entirely of terrigenous minerals: quartz and feldspar (the latter is predominant). In the heavy fractions of the same granulometry, tourmaline, zircon, apatite, and garnet, and single grains of albite, staurolite, epidote, disthene, anatase, amphibole, pyroxene, rutile, barite, magnetite, and hematite have been determined. Authigenic minerals include gypsum and frankolite.

A less investigated amorphous inorganic phase (~20%) consisting of iron oxides and silicon is also present in dictyonemic shales [22]. Fine insets of authigenic pyrite with a content varying 3 to 10% are disseminated throughout the rock.

Dictyonemic shales are extremely poor in faunistic remains. Besides graptolites, which gave their name to these shales (*Dictyonema* genus), rare remains of conodonts and single valves of obolids are sometimes found on bedding planes. At the top of dictyonemic shale beds polished sections reveal single foraminiferal species *Psammosphaera* and *Thurammina* [8].

SOURCE OF ORGANIC MATTER AND ACCUMULATION SETTINGS

The formation settings of dictyonemic shales have been studied little, mainly because the source of organic matter is difficult to determine. Various opinions have been advanced on this point. Some authors believe that organic matter of these shales was generated by graptolites [15, 21, 24]; others interpret it as a product of activity of primitive algae — green, blue-green, and golden algae, dinoflagellates [20], and acritarchs [14].

Our investigations and literary data indicate that organic matter of dictyonemic shales is of a complicated allochthonic-autochthonic nature. We studied the organism which produced autochthonic organic matter in an electron scanning microscope with a Link attachment and in polished sections in an optical microscope with a dark field condenser. The photographs clearly show well-preserved fragments of threads of various diameters, often surrounded by sheaths, which form the bisedimentary microstromatolitic texture of dictyonemic shales.

Colonial *Microcoleus chthonoplastes* is the predominant microorganism. Tubular lithified remains of microcolonies of these organisms in the specimens have a typical diameter of 30 μm , which coincides with *Microcoleus chthonoplastes* colonies in modern basins. Inside the thick common sheath are finer tubular elements of some 10 μm in

diameter. They are comprised of four or five individual threads. A thread can be surrounded by its own thin sheath; the average length of a cell is 4–5 μm , with a width of 3 μm (Fig. 1a, b). In the scanning microscope frequent thin (0.5–1 μm) tubular formations are often seen. These are probably sheaths of green bacteria of genus *Chloroflexus* (see Fig. 1c), which in modern marine basins populate peripheral portions of *Microcoleus chthonoplastes* colonies [25]; tapering *Colothrix* threads are also observed. Their modern relatives have heterocysts and actively fix molecular nitrogen.

Microcolonies of purple bacteria *Thiocapsa* and *Thiocystes* also took part in the formation of organic matter of dictyonemic shales. This is evidenced by the presence in dictyonemic shales of pyritic frambohedra 1.5–2 μm in size, apparently cells from these colonies. A microbial origin of pyrite frambohedra is indicated by their morphologic similarity with microcolonies of purple bacteria and even the presence of these surrounding shells (see Fig. 1d). Published data [30] support this conclusion. Microcolonies settled in abandoned sheaths of filiform microorganisms. The set of cyanobacteria with the dominant *Microcoleus* species observed in dictyonemic shales is typical for smooth aerobic microbial mats that are widespread in shallow-sea littoral-marine settings (the depth is controlled by the limits of the photic zone) — lagoons, bays, and the sublittoral region. In modern conditions, mats similar to that identified in the Pakerot horizon exist in waters of various salinity (from 30 to 200 ‰) and at various latitudes [26]. We have no data to make judgements about the degree of salinity of water in dictyonemic ooze accumulation areas, but there is no question that they were largely desalted. The low salinity is responsible for the presence of *Colothrix* representatives in the cyanobacterial community; their typical habitat is brackish seawater or fresh lake water. The desalinization of dictyonemic basins is also supported by the data of Grabau and Connell, cited by Miroshnikov [16], concerning the finds of normally developed euripterids and phylocardites in graptolitic facies — these are inhabitants of fresh (river) waters.

The desalinization of the basin was largely promoted by a humid climate, confirmed by kaolin found in the mineral matrix of dictyonemic shales.

The productivity of smooth mats with predominant *Microcoleus* is high; in individual cases it reaches 300 mg of organic carbon per hour per 1 m^2 [29], resulting in a high growth rate of microstromatolitic structures. According to some reports [31], the growth rate of smooth stromatolites can be as high as 10 mm/yr = 10 km/1 million years. Adjusting for sediment compaction, sedimentary erosion, and interruptions in sedimentation, the actual rate was much lower. In the Persian Gulf, on the basis of the above factors, it has been estimated at 0.04 mm/yr, or 4 m per 1 million years [32]. Remarkably, the mean sedimentation rate of black graptolitic shales calculated from accumulation rates of graptolitic zones in the Cordilleras (the existence of graptolitic zones was measured by absolute age) yielded the same figure, i.e., 0.004 mm/yr [27].

The benthic microbial coenosis was the main source of autochthonic organic matter for dictyonemic shales, because planktonic microorganisms, which could have been producers of organic matter, have not been found in these specimens.

Besides an autochthonic source, dictyonemic shales received organic matter from an allochthonic source as well. This is indicated by several factors. The classification diagram [33] constructed on the basis of atomic ratios of hydrogen and carbon (hydrogen index) and oxygen and carbon (oxygen index) places the kerogen of dictyonemic shales in the second (intermediate) type, formed of organic matter of an algal as well as terrigenous origin (Fig. 2). Petrographic investigations of dictyonemic shales determined humic gellified inclusions, coaly detritus, and cutinite. The presence of allochthonic organic matter accounts for the high oxygen content in the overall balance of the biomass. Finally, there is a direct correlation between terrigenous silica and C_{org} (Fig. 3); Uspenskii [21]* reported humic acids in dictyonemic shales sometimes as high as 40% of the total weight of organic matter.

Although there is no doubt that allochthonic organic matter is present in dictyonemic shales, its origin is unclear. The difficulty is due to contradictory biochemical data concerning the contribution of land plants to the kerogen of dictyonemic shales and to the prevalent view that at the end of the Cambrian and the beginning of the Early Ordovician there were no higher plants. The fact that the figurative points of dictyonemic shales according to hydrogen and oxygen indices fall in the field of kerogens of the mixed type indicates a contribution of land plants to this kerogen. On the other hand, molecular biological CBA markers show that organic matter of higher plants of a continental origin was not transported to the final basin: there is no clear prevalence of odd homologues in the high molecular region C_{25} –

*Uspenskii interpreted humic matter of dictyonemic shales as an autochthonic material; he considered it to be a product of disintegration of polysaccharide (aminohexose) of the chitin of graptolites that combines the properties of hydrocarbon and protein molecules.

C₃₀ (odd/even = 1.2). The region is not distinct and ends at C₂₈. However, despite this shortening, the content of homologues is high (17.6%; see Fig. 4). Although published data on the possible presence of higher plants even much earlier than the Devonian [5, 7, etc.] resolves this contradiction, doubts concerning their contribution to the organic mass of dictyonemic shales remain.

We think that a more likely source of terrigenous organic matter of dictyonemic shales were microorganisms of freshwater lakes along the edge of the basin on the continent. Disintegration of microorganisms produced humus in lakes. Terrigenous transport then brought them into the marine basin. This hypothesis is supported by Vinogradov's data [4] concerning a high nitrogen content (over 8% of dry weight) in freshwater blue-green algae and Uspenskii's data [21] that humic acids of dictyonemic shales contain a high percentage of nitrogen.

This interpretation of the origins of organic matter in dictyonemic shales explains the high nitrogen content in the organic component. Besides nitrogen influx with nitrogen-containing humus components, the benthic cyanobacterial community itself was conducive to a higher nitrogen content inorganic matter, since it fixed free nitrogen through intensified synthesis of phycoproteins (a pigment-protein complex of nitrogen-containing blue-green algae) in a poorly illuminated environment with aerobiosis.

Dictyonemic shale accumulation is largely associated with the regressive Cambrian—Lower Ordovician sea in the Early Paleozoic Baltic basin, introduced by the general rise of the territory during the Salair folding stage. On the other hand, Pakerot layers clearly reflect littoral settings of a transgressing sea: sandy, obviously shallow-sea sediment (with oblique wavy lamination and interruptions) give way to lithologically consistent silt—clay organogenic entities (dictyonemic shales) of deeper basin parts.

This succession of sediments must reflect a replacement of variable littoral sedimentation environments by more steady sublittoral conditions which persisted throughout the time of dictyonemic shale accumulation. This stability of the facies was supported by tectonic calm in the area of the basin and neighboring territories. Fine terrigenous material was transported from land during that time; compensated low-amplitude slow sagging continued in the meantime in the shale accumulation area. A minor admixture of fine ash in shales [22] was not associated with any volcanic activity in neighboring watersheds. The material was apparently brought from island volcanos in the Grampian geosyncline, situated to the west.

Sublittoral settings favored activity of benthic microbial associations. Most important, detrital matter was brought in small amounts and was unable to suppress the functioning of the mat. Calm sublittoral waters ensured constant water transparency, essential for proliferation of autotrophic microorganisms, as well as for their survival. That waters were calm is evidenced by graptolites living and multiplying in dictyonemic shale accumulation areas; strong currents and wave surf motions would have broken graptolite rhabdosomes and killed them. There are grounds for assuming that the pseudoplanktonic lifestyle of graptolites (attached to algae passively carried around by water) was prevalent because bottom waters were infected with hydrogen sulfide, depriving most of the area of a mat of benthic organisms. It could have been the upper sublittoral region (30–40 m) where the seafloor on small areas emerged above sea level. This fact was responsible for the development of the clay breccia described by Kordikov [13] inside the bed of dictyonemic shales at Maardu deposit.

Accumulation of dictyonemic shales in a sublittoral zone largely matches the picture drawn by Myannil [17] in his paleogeographic map of the Pakerot time of the northwestern part of the East European Platform. On the map, the dictyonemic ooze accumulation area of the Baltic is located to the north of a narrow gulf (or strait), shallow throughout all of its extent (Fig. 5). The shores of the gulf, which applied material to the dictyonemic ooze accumulation area, were mainly clayey and gentle, because these are favorable conditions for life and especially for proliferation of graptolites [19]. Clay minerals were brought into the basin as terrigenous matter from the surrounding peneplain, where blue Cambrian clays were exposed [22]. More distant supply provinces, which provided granular material to the basin, must have been, according to the mineral composition, acid rocks of the Baltic shield.

Organic Matter Decay and Diagenesis

Organic matter decay occurred almost throughout the mat thickness in anaerobic conditions. Aerobic conditions existed only in the first millimeters of the mat, where the organic mass grew. Judging by the enrichment of dictyonemic shales in iron sulfide (up to 50% of reactive Fe), sulfate reduction was a predominant process. Most of the H₂S it produced reacted with iron salts, forming insoluble sulfide and thus protecting the productive part of the mat from being poisoned.

A similar protective function was performed by purple sulfur bacteria, frequent in the intermediate layer at the boundary between aerobic and anaerobic environments. These facultative anaerobic photosynthesizing bacteria oxidized

hydrogen sulfide and deposited large amounts of intracellular sulfur; after the death of an organism, the sulfur interacted with hydrotroilite to form framboidal pyrite.

The pristan-phytan ratio of 0.62 and higher content of ferrous iron compared with the ferric form are also evidence of a reducing setting. Despite this setting, with prevalent sulfate reduction, dia- and catagenetic alterations of organic matter were slight. This is indicated by petrographic studies of the kerogen of these shales (stage PC₃ [1]), the position of the figurative points of dictyonemic shales on Tissot's diagram, etc., the predominance of nonhydrocarbon compounds, such as complex heterosystems in CBA and pyrolytic data — the maximum hydrocarbon yield temperature T_{max} is 421°C, which is lower than maximum temperatures defining the formation zone of liquid oil (430–465°C).

There were two main reasons for the limited destruction of organic matter rapid conservation in lithified sheaths of microorganisms and acidulation of the medium.

Certain data [28] suggest that a partially decayed algal mat becomes lithified at a depth of just 1 cm. A similar situation was likely during the formation of dictyonemic shale, since the three-dimensionality of the threads of microorganisms — autochthonic organic producers — shows that the microstromatolitic texture of the shale was created in an early stage of diagenetic sediment alteration.

Lithification developed on sheaths of live blue-green algae and in the slime on the algae after their death. The alumosilicate shells that enveloped threads as a result hardened rapidly and became an important factor not only for burial of organic matter but also as a "sarcophagus" that made it immune to catagenetic factors.

Al—Si—K composition of the threads of microorganisms suggest a multicomponent system of colloids which replaced the sheaths and sometimes cells of microalgae by alumosilicates. Colloids-sols were formed as a result of vital functions of microorganisms, which processed mineral components brought from land and fine matter transported by eolian routes.

Low acid pH (<7) of bottom water in the basin and its low buffer properties were associated with its initial content of humates, isolation of CO₂, and decay of organic matter, as is usual in dystrophic basins. A drop in pH to 5 and below could prevent further decay of organics, especially allochthonic material, leading to its burial.

The heightened acidity explains the mainly alumosilicate replacement of organics and the virtually total absence of carbonates in the system.

This leads to the conclusion that dictyonemic shales in the Baltic are formations of the sublittoral facies of a transgressing sea basin. The main producers of organic matter in them were benthic microbial organisms, which lived in calm desalinized waters enriched in humic acids of an allochthonic origin. The provenance area of the material was peneplanated land composed of blue Cambrian clays and crystalline rocks of the Baltic shield, where the climates were largely humid.

The destruction of organic matter during diagenesis occurred mainly by sulfate reduction. The limited decay of the organic mass is explained by its rapid conservation in lithified sheaths of microorganisms and acidulation of the medium.

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It is known that the total volume of glauconite in the Paleogene deposits that accumulated in the uplifted areas of syndepositional anticlinal structures of Syria is one order of magnitude greater than the glauconite volume that was deposited on the anticline flank slopes during the same time interval. In the basins, significantly enriched in glauconite, such layers are absent and the total glauconite volume decreased slightly. It appears that glauconite formed in the axial zones of syndepositional anticlinal structures.

Over their entire distribution area, the Paleogene deposits of Syria are represented almost exclusively by calcareous marl rocks. Only in limited instances, as in the eastern border area of the Syrian Desert and the Jebel Bishir Uplift do low-carbonate clays and quartz sand and sandstone lenses occur in the Upper Paleogene [1, 4].

The subject area was a broad marine basin during the Paleogene that occupied the gradually submerged northwestern part of the Arabian Plate. The nearest certainly known land area occurred a few hundred kilometers SE of the Palmyrides (Rutba Uplift, Iraq).

The thickness distribution of Paleogene deposits was determined by the development history of the main structural elements of this region (Fig. 1). The thickness sharply increases in the Syrian platform areas proper (Syrian Desert). In the Anti-Lebanon zone thick sediment sequences accumulated within the Palmyride area, with a thickness one order of magnitude or more than the Paleogene thickness in the platform region.

The Paleogene occurs in practically horizontal beds in the Syrian platform region but in the Palmyrides and the anti-Lebanon Range the Mesozoic and Paleozoic rocks have been dislocated and represent a separate tectonic unit. A few brachyanticlinal fold systems, with orientation subparallel with the axis of the Palmyride trough are the most important in the relief development of the modern Palmyrides. During the Paleogene, the Palmyride anticlinal structures represented syndepositional uplifts on the basin floor. Their crests periodically approached the water surface. This resulted in the formation of carbonate bioherms, located in the brachyanticlinal crest areas in the Upper Eocene. In certain brachyanticlines, these also occurred in the Middle Eocene sections [1, 4].

The glauconite horizons occur in practically all Paleogene sections but their best development was found in the Middle Eocene intervals. They are not ubiquitous but in a number of instances the horizons coincide with foraminifer-based biostratigraphic zone boundaries and their synchronous nature was established at the zone or subzone level (Table 1). Parts of the section under the glauconite horizon are missing in a number of instances. In other sections certain glauconite-enriched horizons have become much thinner.

Composition and Distribution of Glauconitic Beds. The greatest concentrations of globular glauconites occur in certain sands of mixed composition. The size of the predominant portion of the sand fragments correspond to glauconite grain sizes. The concentration range of the glauconite grains is wide (5-30%). Glauconite occurs in nests that enrich certain portions of the sand body (>60%), or is distributed in the groundmass at the 5-8% background level. The glauconitic nests are 0.5-5.0 cm in size phosphorite pebbles that occur in the same sands. A large number phosphate fragments of various composition also occurs in addition to the phosphate pebbles. Various grains form the oolite nuclei, both phosphatized and non-phosphatized types. The relationship between the oolite phosphate shells and nuclei is always preserved due to the predominance of the nucleus, independently of the fact whether the nucleus is a carbonate, glauconitic or phosphatic fragment. No diagenetic or epigenetic growth has been observed in phosphate grains. Each grain, whether coprolite, phosphatized benthic foraminifer or oolite with a nucleus of any composition occurs in the

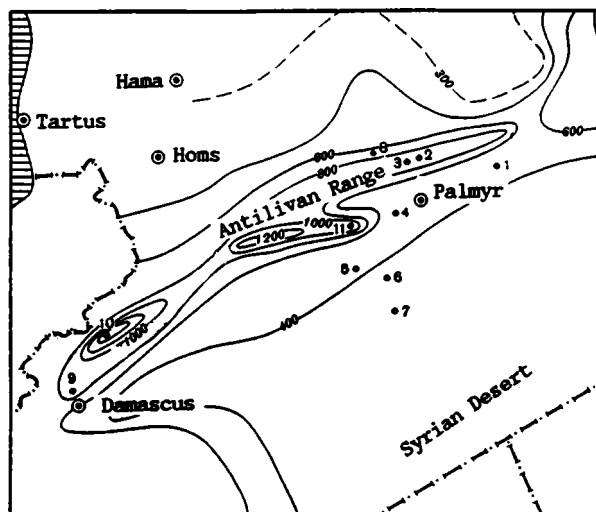


Fig. 1. Thickness distribution of Paleogene deposits in Syria [1, 2]. Sections: 1) Arak (Wadi Harrara); 2) Jabal Antar; 3) Jabal Adiadi; 4) Jabal Haian; 5) Jabal Hohle; 6) Wadi Radir-el-Hamel; 7) Tarak-el-Alab; 8) Wadi Jahar, Wadi Jezel; 9) Maaraba; 10) Maalula; 11) Ain Barde.

sand, without respect to the type of petrographic alteration the grains have undergone. This aspect of the phosphate grains indicates that they formed in the zone where sediments were in transit. Oolite growth did not occur through additional phosphatization after burial. No sandstones occurred with phosphate cement.

Carbonate fragments were also an important component of the glauconite sands. They are represented by large benthic forams or their fragments, molluscan fragments, algal limestones and microgranular carbonate aggregates of unknown origins. Small planktonic forams and coccoliths were absent from the sands. These three sand grain components (glauconite, phosphates and carbonates) represented practically the total sand volume. Quartz in the sands occurs only in certain sections of the Syrian eastern platform region. The relationship between phosphate and glauconite grains differs between different horizons. Certain sands consist only of carbonate and phosphate fragments, or rock fragments in which glauconite predominates over phosphate fragments, while the third, carbonate fragment — component of sandy rocks occurs in all instances (Table 2). It is the indicator of the genesis of the Paleogene sandy deposits in Syria, formed through the reworking planktonic and benthic carbonate sediments of various dimensions. Minor recrystallization of the carbonate detritus in the interstice pores of sands indicates their cementation. The contours of the biogenic fragments, as well as the texture of the enclosing calcite were completely preserved.

The lower boundary of the sandy beds is uneven. The contrast is sharp with the underlying rocks and the underlying rocks were penetrated by tracks of burrowing organisms. These burrows, to a significant degree, were filled by the overlying sediments. The upper boundaries of the beds generally are diffuse and characterized by a gradual decrease in the amount of glauconite and phosphatic matter, along with a gradual grain size decrease of the detrital grains. However, in a number of instances the glauconite-bearing layers are sharply defined in the top portions while the glauconitic matter diminishes within a few centimeters in the section. These beds are underlain by units that became much thinner or disappeared completely from the biostratigraphic sequence. The *Truncorotaloides rohri* Zone is absent in the Wadi Harrar section.

Another glauconite-bearing rock type is represented by slump breccias and fragments that have undergone plastic deformation. In this rock type, the marl blocks are distorted but have not lost their continuity. The sand lenses and nests are isolated, deformed and the glauconite was not dispersed evenly throughout the rock mass. Along with glauconitic (phosphate-glauconite) sands and marl blocks these rocks usually contain phosphorite pebbles, the same size or smaller than the blocks are in the glauconite sands. The sediment texture type is typical of mudflows, slurry flows. This may indicate periodic slumping over the seafloor of glauconite-phosphoritic sediments and nannoplanktonic and nannoplankton and foraminifer muds that have preserved their plasticity and represented coherent layers. The slump displacement of these sediments led to their separation into block, distorted blocks that penetrated parts of the sandy beds within finely dispersed carbonate muds. This process did not lead to the homogenization of the slump flow matter in its entirety, neither to the settling of large phosphorite gravels on the surface of the moving or arrested layers. Each element of such slump flow retained its inherent thixotropic characteristics in each area of the bottom slope it had traveled over. The formation conditions and textural types that evolved during the movement of these high-density

TABLE 1. Location of Glauconitic Horizons in the Sections

Age	Zone classification	Wadi Harrar	Jabal Antar	Jabal Abiar	Jabal Haian	Jabal Hohle	Wadi Radir-el-Hamel	Bir Alejani	Wadi Jahar, Wadi Jezel	Maaraba	Maalula
Oligocene	<i>Globigerina tapuriensis</i> P-18										
	<i>Globorotalia centralis</i> , <i>G. gortanii</i> P-17										
Upper Eocene	<i>Globorotalia cocoaensis</i> P-16			--- (243/83)						--- (22/85)	
	<i>Globigerapsis semiinvoluta</i> P-15	oooo(59/83)		oooo(31/83)		--- (12/85)		 (70/83)	--- (29/85)		
Middle Eocene	<i>Truncorotaloides rohri</i> P-14		oooo(513/84)	--- (238/83) --- (237/83)		--- (11/85)			--- (28/85)		
	<i>Orbulinoides beckmanni</i> P-13	--- (52/83)	 (512/84) oooo(510/84)	--- (30/83)		--- (10/85)		--- (75/83)	--- (27/85) --- (26/85)		
	<i>Globorotalia lehneri</i> P-12	--- (48*/83) --- (45/83)	oooo(509/84)	--- (29/83)	(106/83-κ)	(42/85-κ) (9/85)			--- (85/85) --- (24/85)		
	<i>Acarinina billbrooki</i> P-11—P10	 (42/83) --- (39/83)	 (507/84) (506/84)	--- (233/83) --- (22/84)	(17*/83) oooo --- (17/83)						
	<i>Acarinina pentacamerata</i> P-9	--- (35/83)	--- (291/84-κ)	--- (21/83)	oooo(19/83)						
Lower Eocene	<i>Globorotalia aragonensis</i> P-8						--- (22/85)				
	<i>Globorotalia formosa</i> P-7		--- (287/84-κ)	--- (105/83-κ)							
	<i>Globorotalia subbotinae</i> P-6			--- (117/83-κ)							
	<i>Globorotalia velascoensis</i> P-5										
	<i>Globorotalia pseudomenardii</i> P-4		 (141/84-κ)								
Paleocene	<i>Globorotalia angulata</i> P-3		 (139/84-κ)		--- (67/84-κ) --- (66/84-κ)						
	<i>Acarinina uncinata</i> P-2										
	<i>Globorotalia trinidadensis</i> P-1c										
	<i>Globorotalia pseudobulloides</i> P-1b										
	<i>Globigerina eugubina</i> P-1a										
U. C.	<i>Abathomphalus mayaroensis</i>										

Note: Lithological designations: ooooooooo-gritstones; ----- sandy marls with slump structures;- compressed sediments. Sample number-in brackets. U. C.) Upper Cretaceous.

TABLE 2. Sand Composition, in %

Rock designation	Sample No.						
	19/83	31/83	59/83	17 ^a /83	509/81	510/81	513/84
Glaucanites	13	22	7	32	24	1	45
Phosphates	20	4	2	25	21	72	17
Carbonate fragments	67	74	91	43	55	27	38

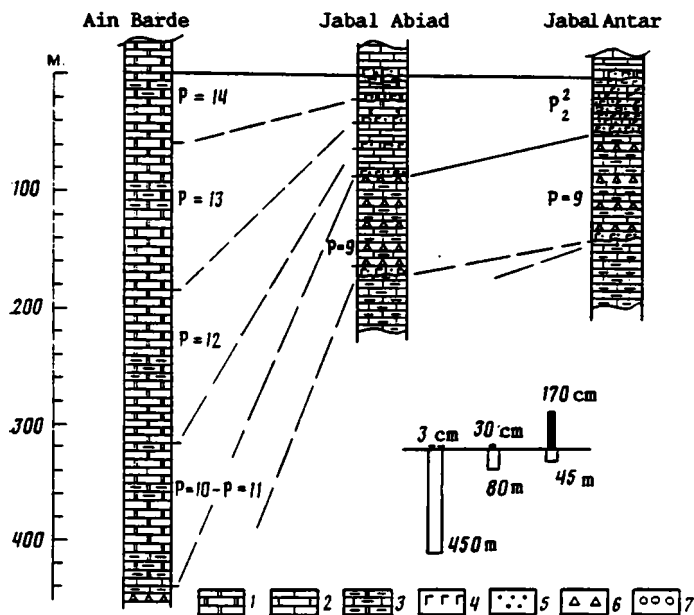


Fig. 2. Middle Eocene sections in the flexure zone, on the structural limb and in the axial zone of syndepositional anticline. Total glauconite volumes in the correlated sections: 1) Chalky limestones; 2) limestones; 3) clayey limestones or clayey chalky limestones; glauconite; 5) granular phosphorites; 6) silica; 7) phosphorite conglomerates.

currents have been described in sufficient detail [6]. Depending on the mineral composition and the relationship between fragments of different size, as well as the water content in the muds, downslope sediment movements had been initiated at different bottom slope angles. Earthquakes may have had an important impact on the process. Glauconite-bearing layers represented rocks with plastic sedimentary slump structures in most of the studied sections.

Sharp lithological contacts exist at the base of these beds. The underlying sedimentary units became either condensed, or are completely missing. The absence of the *Globigerina eugubina* zone occurs under the basal bed of the glauconitic marls in the Maalud, Jabal Haian and Wadi Johar sections. The absence of a significant portion of the Paleogene and Lower Eocene intervals was noted beneath the basal glauconitic marls in the Wadi Radir-al-Hamel section.

The absence of certain zones under the basal glauconitic horizon at the base of the *Acarinina pentacamerata* Zone in the Jabal Adnan section is of special importance. All the Lower Eocene zones are absent here. 150 m from this section in an adjacent gully of Jabal Adnan, however, the basal glauconitic horizon of the base of *Acarinina pentacamerata* zone directly overlies marls of the underlying *Globigerina aragonensis* zone across a sharp, lithologically defined erosional unconformity. The lower Eocene section that survived erosion is c.50 m thick. This configuration may only be explained by effects of underwater slumping at certain sea bottom locations. Apparently, the underwater landslide events there preceded accumulation of glauconite-bearing rocks at the base of the *Acarinina penmtacamerata* zone. A slight corrugational deformation of the structure's limb and truncation of the highest portions in the monocline may also have happened in this case.

In addition to the discussed glauconitic horizons, the Syrian Paleogene sections also contain marl rock units with large quantities of fine biogenic carbonate matter (including planktonic and benthic forams), phosphate and glauconite grains. These rock units occur in the underlying deposits without apparent indications erosion and only with minor

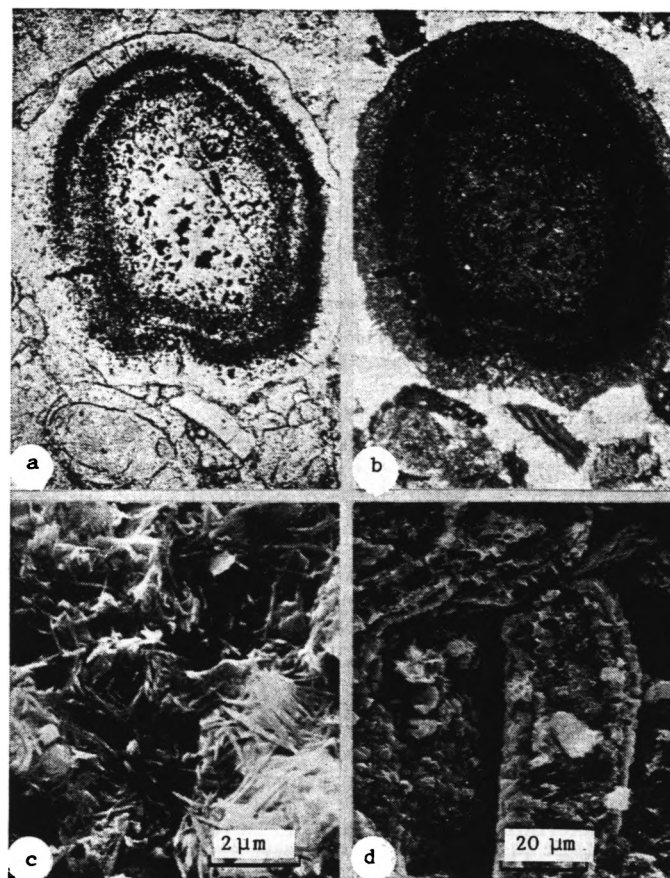


Fig. 3. Heterogenic glauconite grains. Sample 19/83: a) glauconite grain photomicrograph with concentric distribution of goethite blobs, $\times 90$ magnification, parallel nicols; c) goethite inside glauconite grain (SEM); d) sample 20/83, glauconite-phosphate grain fragment, hexagonal francolite flakes, globular collophane incrustation (SEM).

TABLE 3. Glauconite Distribution, Based on Density Fractions, in %

Fraction No.	Density g/cm ³	Sample No.					
		20/83	66/84	19/83	17/83	59/83	31/83
1	<2,4	<1	1	None	<1	Trace	4
2	2,4—2,5	25	10	—	15	<1	45
3	2,5—2,6	47	13	—	47	9	23
4	2,6—2,7	22	39	Trace	23	58	17
5	2,7—2,8	5	35	3	12	29	8
6	2,8—2,9	<1	1	4	2	3	2
7	>2,9	<1	1	93	<1	1	1

tendency toward an increase in the coarse component content of marls. This may suggest an increase in the hydrodynamic energies in their area of formation. The glauconite content of these horizons is significantly low. Usually it equals or is less than a few percentages of the rock volume. These horizons reflect a very abrupt thinning of the correlatable stratigraphic subdivision. The thickness values of the glauconitic marl vary widely. Thus, the marls exceed 12 m in the Middle Eocene of the Jabal Haian section. In other sections, the dispersed glauconite and marls occur in intervals, ranging in thickness from a few centimeters to 4 m. The presence of glauconitic marls is typical of the most condensed Middle Eocene section in Jabal Antar. In this c.40 m thick Middle Eocene section, a cumulative total of 20 m sand occurs in various beds that overlie sharply defined erosional surfaces. The rest of the section is composed of coarse marls with disseminated glauconite grains. Benthic foraminifers only occur among the fossils. Upward in the section these rocks either display continuous alternation phosphate-glauconite sands or are in quite sharp

TABLE 4. Chemical Composition of Globular Glauconite, in %

Components	Fraction No.						
	3 (20/83)	5 (66/84)	7 (19/83)	2 (17/83)	4 (17/83)	4 (59/83)	4 (31/83)
SiO ₂	49,33	49,92	20,58	41,32	46,21	46,81	44,34
TiO ₂	—	0,07	0,12	0,20	0,20	—	0,16
Al ₂ O ₃	8,81	7,11	2,81	7,55	6,79	8,94	7,72
Fe ₂ O ₃	14,39	17,97	7,62	13,53	18,04	17,84	15,97
FeO	0,99	0,79	0,48	0,08	0,53	0,37	0,26
MgO	4,20	5,06	2,30	5,26	3,99	4,14	4,02
CaO	2,90	1,61	30,51	7,60	5,04	3,70	4,68
Na ₂ O	0,17	0,25	0,95	0,45	0,23	0,14	0,23
K ₂ O	6,40	7,38	2,58	4,85	7,44	6,86	6,76
H ₂ O ⁺	6,14	5,10	4,10	6,71	4,45	3,23	7,20
H ₂ O ⁻	3,94	2,35	1,25	6,84	3,75	4,56	4,83
CO ₂	—	0,49	3,02	4,66	0,89	1,64	0,88
C	0,44	0,25	0,50	0,11	0,38	—	0,44
P ₂ O ₅	1,47	1,00	21,56	1,21	1,87	1,48	2,00
	99,18	99,35	98,32	99,37	99,81	99,71	99,49

Note: Sample numbers in brackets.

contact with the sands proper. They differ from those sands by their significantly altered petrographic textures. Such deposits may be termed "condensed type"; these sediments formed during uninterrupted deposition, under high-energy hydrodynamic conditions.

We now review the structural geological aspects of the Paleogene sections in question. Two factors are considered in the geomorphological setting of the described sections. First, each positive structure was synchronously uplifted within the relief of the range. Second, the mineralogical stability and resistance to erosion differ significantly throughout the structures. Massive Oligocene limestones in the top of the Paleogene sequence formed protective cuestas, while softer Eocene and Paleocene marls occur at identical hypsometric elevations in the anticlinal axial zones. Such differences in rock resistance predetermined the position and development of the median valleys in each anticlinal structure, cut across the anticlinal axis. The cuesta relief sharply outlined these valleys. If sturdy, recrystallized older Maastrichtian rocks became exposed in the anticline centers, then these now form the central ridge. Paleogene sediments of the anticlinal crest areas underwent erosion; presently these occur only in sections within the anticlinal limbs. Therefore, glauconitic marls with slurry (high density) flow structures are the most widespread in these sections.

The stratigraphic subdivision thickness patterns perfectly fit the location pattern of the section locations in the axial zones of the anticlinal folds. A sharp thickness reduction occurred in the various biostratigraphic zones in areas adjacent to the anticlinal fold axis zones. The Paleogene zones generally thicken away from the anticlinal structures (Fig. 2). This is apparent from the comparison of the Ain Barde sections (at some distance from the anticlinal axis) and the Jabal Adiad and Jabal Antar sections. The Jabal Antar section is located in an uplifted area of more better expressed topography, a part of certain anticlinal structures. This thickness distribution pattern indicates syndepositional growth of the Palmyride and Anti-Lebanon structures. Formation of syndepositional sediments and sands in the uplifted parts of condensed structures (Jabal Antar) may indicate times of maximum uplift or even the exposure of the anticlinal crest zone to water erosion. During the same time interval slump breccias, including plastically deformed landslide blocks of marls, formed with incorporated glauconite sands on the slopes of syndepositional tectonic structures. Thus, the Middle Eocene Jabal Antar section includes six erosional surfaces over which sand beds have accumulated. The other side of the anticline in the Jabal Adiad section displays only one Middle Eocene glauconite—phosphorite—carbonate sand bed in the top Middle Eocene unit. However, the Middle Eocene section here contains six marl units of various amounts of glauconite and with landslide structures.

Should these levels in the Jabal Adiad section be defined with the precision of a zone with the help of planktonic foram stratigraphy, the Jabal Antar section, due to the absence of small planktonic fossils, would represent but a single Middle Eocene interval.

The thickness values of glauconitic horizons may be established in an overall correlation, involving comparison of the section positions with that of the anticlinal axis zone. However, change in the sedimentation regime did primarily influence the composition of accumulating sediments. With the decrease of the total sediment thickness in the anticlinal crest area, sand played the most important role in the rock composition. Glauconite was one of the three main sand components. Recalculation of the sediment thickness, so as to account only for the total thickness of glauconite in glauconite-bearing beds and the background quantities in limestones and marls (glauconite was absent in these deposits, or represented but few hundredths of one percent) led to the recognition of a close interrelationship between the maximum total glauconite accumulation rate and the maximum thinning of a given stratigraphic interval. Thus, 40–45 m sediment accumulated in the Middle Eocene Jabal Antar section. More than 20 m of this interval was represented

by glauconitic sands. The recalculated thickness of pure glauconite was only 1.7 m. This indicates a glauconite sedimentation rate of c. 340 g/cm³ during the Middle Eocene. In the adjacent Jabal Abiad section the sediment accumulation during the same period was 80 m. The total thickness of glauconite-bearing sediments there was 5.25 m. These were represented essentially by glauconite-bearing marls, with landslide structures. They contained much more sand than glauconite. Recalculation to pure glauconite content provided a figure of c. 30 cm, corresponding to a deposition rate of 60 g/cm³ during the Middle Eocene.* In contrast with the Wadi Ain Barde section, located in the limb area, at a significant distance from the structural axis, this section contains no glauconitic sands and marls. Individual intervals of the section were enriched in fine glauconite but its concentrations did not exceed a few hundredths of one percent. The Middle Eocene section of Ain Barde is c. 450 m; while the recalculated total, pure glauconite thickness c. 3 cm, or the accumulation rate maximum 6 g/cm³ during the Middle Eocene (Fig. 2). In comparing these values it should be considered that a significant part of glauconite (basically, the finest grains) has been eroded during the uplift of the raised parts of the structure. Corresponding figures for the Jabal Antar section are much lower, in comparison with the actually formed (but not preserved) glauconite volumes in this region.

Mineral Composition of the Rocks. The carbonate portion of the dominant limey and marly rocks in the Paleogene are composed essentially of organogenic calcite. The calcite fragments of the calcitic detritus have been altered due to the structural facies conditions of the sections. Coccolithophores, planktonic forams, and submicroscopic calcite crystal particles, most likely remains of planktonic organisms, occur among the carbonate fragments, in the downwarped, pelagic zone of sedimentation. In the Paleogene and Lower Eocene intervals individual authigenic dolomite grains, 3–10 µm in size were also present as admixtures. In a few beds the dolomite content reached 30%. Two such layers occur in the Upper Paleocene Ain Barde section. The admixture of rare dolomitic incrustations occurred in all Lower Eocene and lower Middle Eocene zones (zone ones P-10, P-11). Dolomite is absent from the upper part of the Middle Eocene and the Upper Eocene.

Palygorskite and montmorillonite dominates the insoluble fraction of the carbonate rocks (10–45% of rock units). The mineral ratios were variable. In the upper part of the section, the *Globorotalia lehneri* interval, where dolomite is absent, the insoluble fraction of a marl layer contains 80% palygorskite. This zone occurs in the most subsided portion of the central Palmyrides.

Powdery quartz that can not be identified in the coarser fraction is always present in the aleurolitic and pelitic fractions (2–50 µm) of the insoluble carbonate rock residues. In a number of stratigraphic settings (between the Upper Paleocene and upper Middle Eocene) one finds open primary pore spaces in foraminifers, partially or completely filled later by chalcedony. This allows tentative quantitative evaluation of the powder quartz admixture through the diffraction data. A certain (possibly, significant) portion of this admixture may be associated not with the finest, eolian detrital quartz grains but with chalcedony of authigenic origin.

The insoluble residue composition is somewhat more variable in the slumped marls, that were enriched in glauconite and phosphates. After standard treatment (rock sample dissolved in 10% acetic acid) clay minerals accumulated in the fine fractions of the residue. These minerals (palygorskite and montmorillonite) are typical of the subject area. Illite admixtures that indicate the presence of glauconite, are also always present. This is confirmed by increased illite peak intensities in the 3–5 and 5–10 µm fractions, indicative of dioctahedral, iron-bearing varieties. The quartz concentrations, as identified through diffractometry is somewhat greater in these fractions but the bulk of the matter belongs to the phosphates. Thus, the glauconite-enriched marl rocks and glauconite-free marls, when fragmented, contain the same mineral components in their fine silty and pelitic detrital fractions. The sand fractions contain mineral fragments of the glauconite—phosphorite—carbonate sands.

The insoluble residues of the sandy (glauconite-phosphate-carbonate) rocks consist of 80–90% authigenic grain fragments (glauconite, phosphate) and granular syngenetic organic substances (biomorphous phosphate or phosphatized fragments). The concentrations of illites (glauconites) increased in the silty and coarse-pelitic portion of the insoluble residues but glauconite dominates the pelitic fraction proper (<2 µm). The montmorillonite-palygorskite mixture was preserved. Diffraction patterns of the pelitic fraction of these rocks always indicated a halo in the 8–14 Å area, sometimes identified as goethite. The presence of goethite was fully expected; the petrographic study of sands has already indicated the constant presence of iron oxide coagulates; either slightly tinting individual areas in the thin sections, or representing fragments of individual mineral structures. In addition, iron oxides often occur in concretions with glauconite grains. Such concretions can not be interpreted as products of later glauconite weathering and disintegration: the same rock contains completely unpigmented grains, grains with zonal pigmentation, and grains with mottled pigmentation, related to fracture systems within glauconite (Figs. 3a, b). The SEM-study of such grains indicated that goethite that occurs with glauconite in individual globules is always isolated as spherical precipitates of

*Survey of measured section. Mapping data indicates that the Middle Eocene at Jabal Abiad is 120 m thick.

uniform size (former colloidal spherules). The periphery of the goethite globules was occupied by a complex, consisting of concretions and fan-shaped aggregates of elongated goethite crystals (Fig. 3c). Apparently, the nonstoichiometric composition of the gel, with an excess of iron, led to the goethite-glaucinite mineralization and formation of isolated goethite coagulates and pigmented films in the sands. The dissolution of the most finely dispersed goethite particles in acetic acid apparently almost completely eliminates this rock component from the pelitic fraction in the insoluble residue. In addition, the mechanical and chemical stability of the globular glauconite particles prevents the dissolution of the goethite coagulates that are enclosed in the glauconite. Goethite inclusions in glauconite seriously hamper interpretation of its chemical composition.

The nonuniform composition of glauconite grains is also indicated by the zonal or mottled distribution of their Ca-phosphate content (Fig. 3d). It forms either margins around the grains or occurs inside the grains as films, coagulates or small oolites, that grew by rolling around in the protoglaucinitic gel. Forams tests also occurred within the glauconite grains. Their centers were filled by Ca-phosphate. Such grains occurred in all samples but most often the glauconite-phosphates occurred beneath the *Acarinina pentacamerata* Zone. This condition led to a sharp weight increase of the glauconite grains, reaching a maximum of 2.9 g/cm^3 (Table 3) on the density chart; the presence of goethite could not directly be established from the chemical analysis or glauconite density data. The globular goethite precipitates within the glauconite grains measured 2-3 microns. For this reason, only coagulates of these precipitates could be identified by optical methods (Figs. 3a, b).

The investigated mineral paragenetic stages indicate an equal predominance of oceanic matter in the makeup of the three rock types. This matter essentially represents the total rock composition in the described Syrian Paleogene units. The detrital matter is essentially limited by the paleorelief of each specific basin floor area. Only a sharp increase in the quantity of glauconite in the uplift areas of syndepositional anticlinal structures indicates possible detrital source areas. The dominance of sands and gritstones in the anticlinal axial zones and their uniformly low fine fraction content indicate that huge quantities of the sediments, formed in shoal-bank areas have been eroded and transported to the limb zones of the folds; to the deepest areas of the adjacent marine basin. This also applies to carbonate detritus, phosphate fragments and glauconite. The cited estimates of the glauconite volume that formed and accumulated in various structural positions of the marine basin may only be sharply reduced for bank surface areas that underwent maximum simultaneous erosion. Consequently, glauconite formation occurred continuously and periodically in crest zones of syndepositional anticlinal structures. The greatest glauconite volumes were deposited on abrasional erosion surfaces or over surfaces eroded through the landslide activity of slumping sediments. This configuration of the main glauconite mass indicates only times of great periodic intensification in glauconite formation. Periods of intensive glauconite accumulation immediately followed period of the uplift of axial fold zones and changes in the inclination angles of the anticlinal limbs. Such extreme conditions have been directly detected by the comparison of thickness values of glauconitic and glauconite-free rocks in the periphery of uplift zones. Here, the thickness of glauconite-free rocks in a given time interval was tens of meters thick, while correlative glauconitic marls measured only several tens of centimeters. The difference is two orders of magnitude. The deposition rates of glauconite-free carbonate sediments ranged between $1\text{--}3 \text{ cm}/10^3 \text{ yr}$. The rate, calculated only for glauconite deposition was on the order of several hundredths of one millimeter per thousand years. This value is only tentative due to the uneven glauconite distribution throughout the section. In uplift areas the preserved (uneroded) glauconite volumes accumulated one order of magnitude faster, while carbonate settled one order of magnitude slower than in the slope regions of the structures. If times of decreased carbonate accumulation rates are completely explainable by a continuous and periodical erosion, the accumulation of a certain glauconite ratio may only be explainable by a steady and discrete introduction of large quantities of Si, Fe, and Al in the axial zones of the anticlinal structures. Periods of sharp increases of these components immediately followed uplift periods of the anticlinal axial zones. Consequently, seafloor supply of highly mineralized solutions, rich in hydrolyzate elements may be the only possible glauconite source. Only this instant hydrolyzate surplus, in the form of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, SiO_2 , and $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ -gels, blobs.

The constant presence of globular goethite in glauconitic concretions indicates a constant iron excess in a nonstoichiometric composition of the parent gel matter. A certain reduction in the goethite content in the glauconitic marls on the uplift slopes may be related to the greater density of iron hydroxide coagulates and, as the result, to their lesser mobility at a given water current velocity.

The phosphate distribution pattern, in terms of total volumes and their detrital composition, suggests two important characteristics. The largest bone fragments accumulated in zones of the greatest hydrodynamic activity. In addition, phosphatic gritstones and conglomerates occur in the uplifted shoal areas. The composition of the pebbles is essentially identical with that of the oolites. If the oolite nuclei contain a given sediment component (foraminifers, shell detritus, glauconite grains, etc.), then the gravel fraction of the phosphates always contains a very thin coating of apatite film (of a fraction of a mm) that envelops the entire fragment. The nucleus of the fragment may be filled either by a large (pebble-size) molluscan fragment, or the lithified phosphatic, phosphatic-glaucinite, phosphatic-glaucinitic-

-carbonate sandstone. At the same time, a glossy, encrusting apatite film may also cover the phosphate pebble surfaces and an abundance of gritstone and sand grains and oolites of the previously described petrographic composition. Consequently, latification of the phosphate matter proceeded swiftly and each cycle of decomposition, fragmentation and transport of the rock fragments was accompanied by the formation of films, encrusting the newly formed fragments and by cementation of the sedimentary particles at a given depth. May this be related to the formation of phosphatic fragments of peculiar composition and the absence of glauconite of similar characteristics? Let us consider now the phosphate group in the coarsest layers (conglomerates, gritstones) and the phosphate and glauconite mixtures in the sands. Apparently, from the moment of their formation, the coarsest sediments were not involved in glauconite formation, or the lithification of the protoglaucinitic gel occurred much slower than sediment lithification during phosphate cement development. In the first case, the protoglaucinite gel clots did not form during the maximum uplift stage of the tectonic structure, while in the second, they disintegrated in water and were transported beyond the formation zone of gravels and conglomerates. Both variants that may account for the differences may have taken place. However, one vital circumstance suggests a preference for the first variant. If one follows the formation process of granular sand marls over the slope area of the structure and the subsequent compositional changes of the sands in the crest areas, one is impressed by the variable quantities of phosphatic fragments in all glauconite-bearing sands and marls and by the presence of phosphatic sands and phosphatic marls with sandy nests that are almost devoid of glauconite. Consequently, the hydrodynamic regime alone may not account for the formation of all phosphate rocks (although high-energy hydrodynamic conditions may form pure phosphate pebble concentrates).

In addition, glauconitic sands appear above the erosional surface and are intrinsically included into the lower portions of the overlying rocks. Formation of phosphatic-gravel rocks and phosphate conglomerates indicate times of maximum uplift in the axial zones of structures but not periods that immediately followed them. We believe that this circumstance again confirms the conclusion of the separate nature of the beginning of solution activity. These solutions contained large quantities of hydrolyzate elements (Fe, Si, and Al) during a long time period during the formation of the phosphorites proper. At any rate, the existence of phosphatic (phosphatic-carbonate) sands proper indicates the absence of significant amounts of protoglaucinitic gel clots in the sediments during these times.

The study of the composition of Paleogene deposits indicates that the dominant rock volume of the Paleogene in Syria formed in marine (biogenic carbonate) facies. Terrigenous matter had practically no influence on sediment deposition.

Facies differences of the deposits were due to syndepositional tectonic regimes, within large individual structural units or by separate areas of anticlinal or synclinal folds. The tectonic regime had a twofold impact on the type of deposition. On one hand, syndepositional growth of tectonic structures influenced the seafloor, the bottom slope inclination at various seafloor locations, the proximity of anticlinal crests to sea surface and, as the result, the hydrodynamic impact of the water at each given location. On the other hand, the revival of tectonic activity also increased hydrothermal-exhalational activity in fault zones, especially in the axial zones of anticlinal structures. The total glauconite volume that accumulated in the uplifted areas of syndepositional anticlinal structures within the same geological time unit is two orders of magnitude greater than the glauconite volume that accumulated in distal monoclinical areas. Thus, the characteristics and spatial orientation of tectonic movements controlled the supply of rock volumes into the depositional basins, primarily by the transport of large volumes of element-hydrolyzates to the basin floor. This process led to formation of protoglaucinitic gels. The introduction of Fe and Al greatly increased during times of the introduction of Fe and Al greatly increased during times of the fastest anticlinal uplift and occurred in the axial zones. The model of glauconite formation in the syndepositional Palmyride uplift areas is similar to the glauconite formation model, established earlier in platform-type glauconitic-siliceous formations [3], flysch formations [5], and over underwater volcanic mountains [2]. The similarity between these models indicates the existence of a protoglaucinitic gel that had formed only at the contact between highly mineralized solutions and sea waters.

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ROLE OF EPIGENETIC PYRITIZATION IN THE DEVELOPMENT OF URANIUM

METALLIZATION ON INFILTRATIONAL DEPOSITS

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An infiltrational uranium deposit is described which includes ores associated with syngenetic and epigenetic reducers. In the latter case, the reduction barrier is near-fault zone of epigenetic pyritization formed during two stages of activity of rising hydrogen sulfide solutions superimposed on preoxidized rocks.

Infiltrational uranium deposits are formed by oxygenated formation water or groundwater in a medium containing effective reducers. Two genetic varieties are often distinguished according to the reducing agents of such deposits [1, 4, 10-12]: 1) deposits in rocks with syngenetic reducers (peat, lignites, coal, and coalified vegetable remains), and 2) deposits in rocks with epigenetic reducers (bitumens, hydrogen sulfide, and hydrogen of biogenic, abiogenic, and mixed genesis).

The authors investigated an infiltrational deposit where the two rock varieties coexist; the position of the uranium metallization on the boundaries of oxidation zones of different ages in the former case is controlled by the distribution of coaly organic matter; in the latter, by signs of intense near-fault epigenetic pyritization of sandy rocks.

The deposit is located in the northern margin of an orogenic body which during the Mesozoic and the Cenozoic evolved as a negative geologic structure with specific features of sedimentation, diagenesis, and subsequent alteration of sediments.

The rocks of the sedimentary cover filling the depression consist of two formations, representing two stages in the region's tectonic evolution. The lower formation is of a platformal type; it is variegated and terrigenous and consists of alluvial, deluvial, and proluvial sandy oligomictic and silt-clay unarticulated Upper Cretaceous—Lower Oligocene sediments, occupying the lows in the Paleozoic ancient relief. Transgressively, with a broad overlap of earlier sediments, it is overlain by a suborogenic formation of red and brown small-detrital Middle Oligocene—anthropogenic molasse comprised of sand—clay lacustrine, deluvial, and proluvial accumulations.

The onset of the orogenic stage in the area's development is recorded by a regional interruption in sedimentation, the formation of an ancient pre-Middle Oligocene leveling surface, and the appearance of coarse-clastic gritstone horizon.

The abrupt intensification of differentiated tectonic motions occurred during the Middle Pliocene and Late Pliocene—Quaternary; it raised the mountains surrounding the depression and exposed the Paleozoic basement in some areas, with the formation of intradepression rises.

A typical feature of Mesozoic—Cenozoic sediments is the facies replacement of virtually all alluvial sediments in the depression margin by deluvial—proluvial red rocks, indicating a possible prolonged development of oxidative epigenesis in adjacent parts of the section consisting of gray rocks.

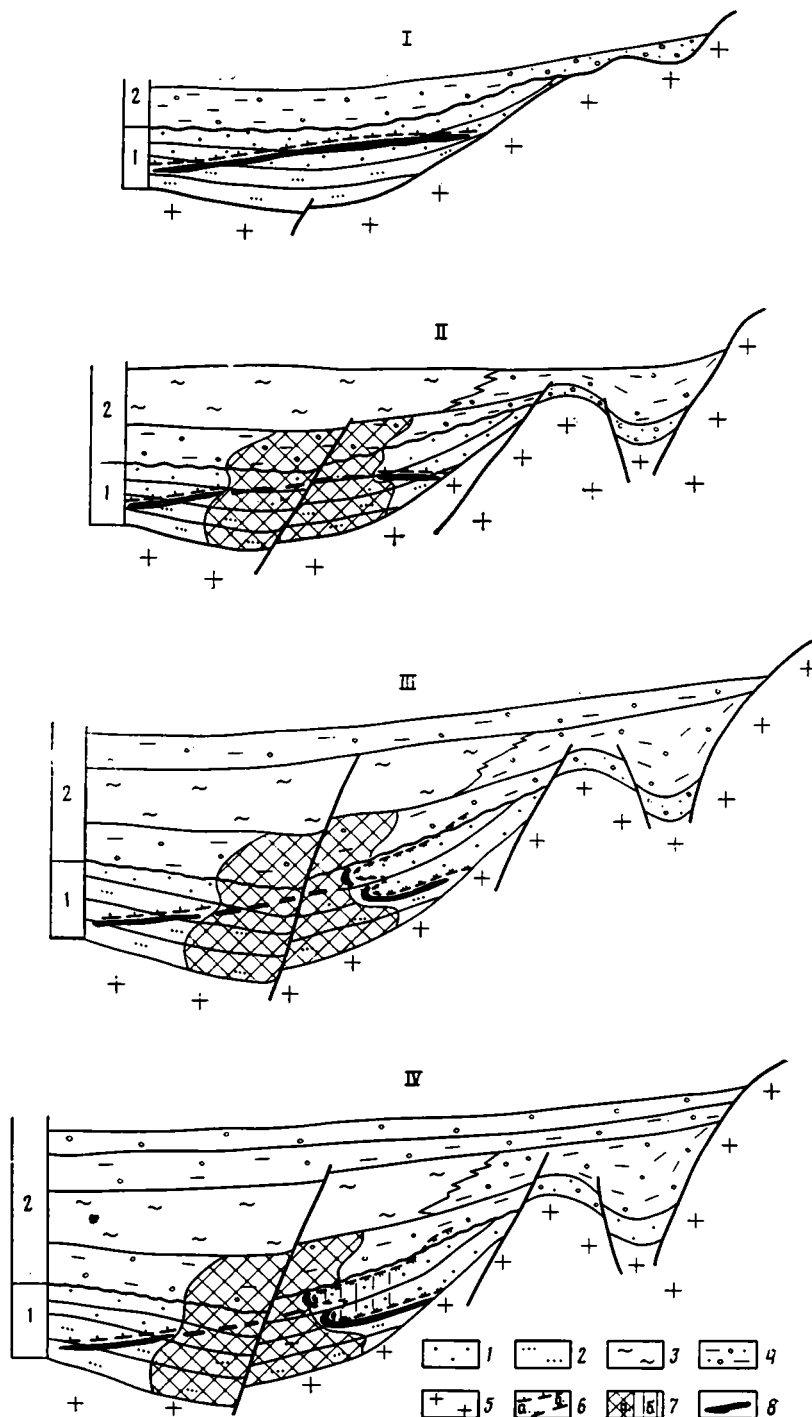


Fig. 1. Stability (I-IV) of mineralization processes: 1-2) primary gray sediments (1 — medium- and coarse-grained sand, 2 — small- and medium-grained sand); 3-5) primary red sediments (3 — clay, 4 — sand-clay rocks, 5 — Paleozoic basement rocks); 6) boundaries of oxidation zones (a — in-ground-infiltrational stage I, b — bed-infiltration stage III); 7) secondary reduced rocks (a — stage II, b — stage IV); 8) metallization. Numbers in the figure indicate: 1) lower bed (formation of gray oligomictic sandstone); 2) upper bed (formation of red and brown molasse).

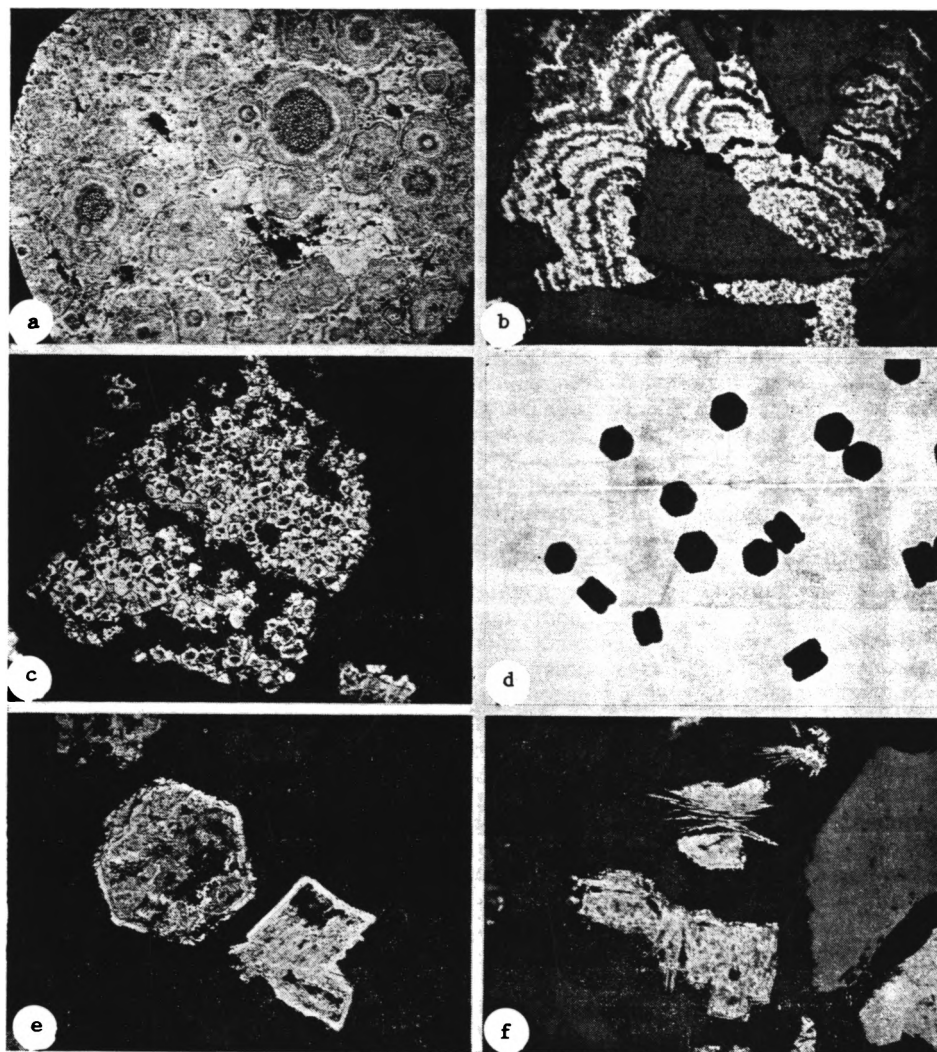


Fig. 2. Morphologic types of pyrite: a) micronodular small- and coarse-crystalline pyrite type I, magn. $\times 500$; b) concentrically zonal aggregates of cryptocrystalline pyrite type III, magn. $\times 160$; c) fine and small crystalline pyrite type IV, magn. $\times 630$; d) hexagonal pyrite grains type V, magn. $\times 200$; e) same, transverse cross section of prisms, magn. $\times 630$; f) same, lengthwise cross section of prisms, fine pletelets seen between the prisms, magn. $\times 630$ (a,b,c,e,f — in reflected light; d) in transmitted light).

Structurally, the area of the deposit is confined to an elevated block of the Paleozoic basement, lying 1500–2000 m above the rest of the northern side of the depression.

Its relief includes outcrops of Paleozoic massifs separated by a submeridional stretched saddle compounded by zones of long-lived flexural-rupture faults. This predetermined the chemical abnormalities of the Cretaceous–Paleogene aquifer groundwaters. On most of the territory of the depression, down to a depth of 2000 m, formational water is characterized by a low salt content (0.3–0.6 g/liter) and a high oxygen content (4.6–10.6 mg/liter); its composition is hydrocarbonate-sodium with the redox potential of +224 to +492 mV — evidence of deep infiltrational flushing of the sedimentary cover and a regional spread of oxidative hydrogeochemical settings. On the deposit itself the waters become slightly hydrogen-sulfidic, and sulfate-chlorite-sodic, with SO_4^{2-} ions of more than 1000 mg/liter, and a total salt of 4–5 g/liter or more. This water is a mix of infiltrational water and rising fissure solutions from tectonic fault zones supplied from the Paleozoic basement. This latter water is devoid of oxygen and enriched in hydrogen sulfide and

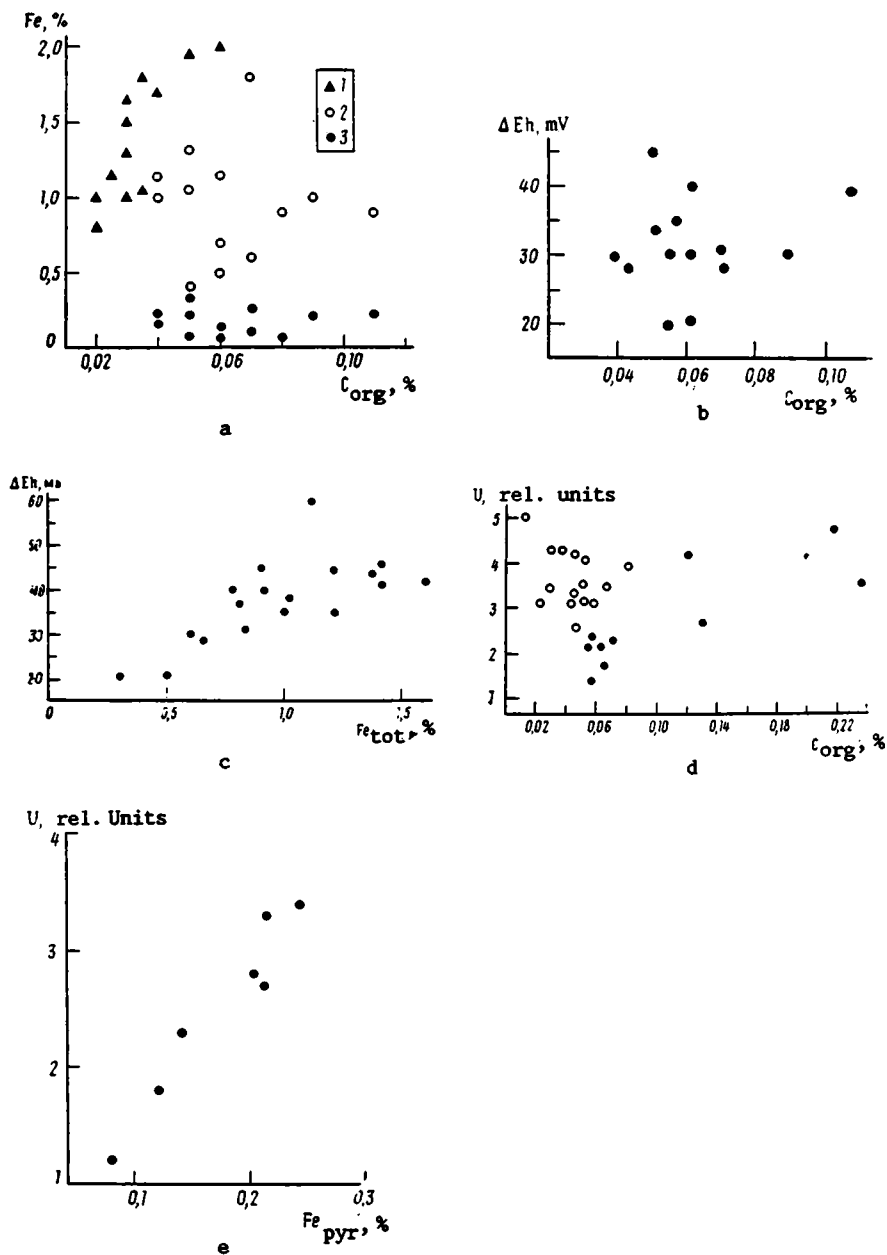


Fig. 3. Ratios of geochemical parameters of ore-enclosing sediments: a) relation of Fe and C_{org} (1 — Fe_{gross} vs C_{org} in other ore bodies, 2 — same in the deposit investigated, 3 — Fe_{pyr} vs C_{org} in the deposit studied); b) relation between Eh and C_{org} ; c) ΔEh vs. Fe_{gross} ; d) U vs C_{org} (open circles: lower member; solid circles: upper member); e) U vs Fe_{pyr} in upper member.

hydrogen; it has a high salt content (20 g/liter). Recent foci of mineralized water discharge are seen in numerous rising sources along terrace ledges and exposures of Paleozoic rocks.

The influence of rising reducing solutions is seen in the high degree of pyritization of sediments, often not justified by sediment accumulation or diagenesis conditions. The pyritization zones appear as "foci" tending to concur with intersection nodes of long-lived faults. A higher pyrite content is observed not only on gray alluvial layers of the lower terrigenous formations but also in the red molassoids of the upper formation, appearing as a superimposed sulfide mineralization. Given the ancient inherited nature of the flexural-rupture faults that existed here already during Cretaceous sedimentation, the activity of rising hydrogen sulfide solutions may be traced back to the time of formation of the sediments of the lower (platformal) strata and to continue even to the present time.

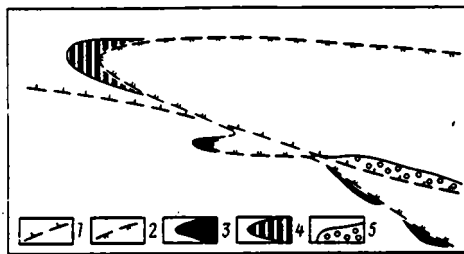


Fig. 4. Relations of the boundaries of ancient in-ground-infiltrational and young bed-infiltrational oxidation zones: 1) lower boundary of ancient in-ground-infiltrational zone; 2) boundary of young bed infiltrational zone; 3-4) metallizations (3 — associated with syngenetic reducers, 4 — epigenetic reducers); 5 — areas of past locations of metallization associated with syngenetic reducers.

The ore is surrounded by oligomictic sediments of platformal terrigenous formations, dated as Cretaceous-Paleogene. They are from 60 to 140 m thick. The thickness increases from the perimeter to the center of the deposit (Fig. 1).

Rhythmic members consisting of two or three sedimentation rhythms are seen in the section. The lower and middle elements of the rhythms are composed of relatively coarser matter; basal layers include numerous boulders and "shreds" of silt-clay rocks. The roof of the rhythmic portion consists of clayey siltstone with interlayers enriched in fine coalified vegetable detritus or brown coal, up to 3 m thick. The presence of the coaly matter is also observed in the sandy sedimentary varieties. Intraformational erosions complicating the general sedimentation sequence are widespread.

Accumulation of the ore-enclosing sediments within the area of the deposit took place in beds of rivers and temporary streams, floodplains, bayous, lakes, and swamps. The northern margins of the depression during the Meso/Cenozoic were stable areas of elevation and erosion where proluvial, variously detrital, or fine-earth red rocks were formed.

The Cretaceous-Paleogene is characterized by a coarsening of the rocks down the section associated with the general rise in the intensity of tectonic motions. The lower two members display a highly dispersed terrigenous sedimentation and increased quantities of coaly matter. They are found in the lows of the Paleozoic basement, filling the uneven elements of the ancient relief. In the upper two members pebble-gravel conglomerates are interstratified in lenses; there are inequigranular sands and sandstones with siltstone and clay interlayers, resulting in a pronounced lithologic anisotropy. Coaly detritus is less common; in member IV it is absent. Relicts of primary red pigmentation of rocks and segregates of brown iron hydroxides are not uncommon.

In the Cretaceous-Paleogene section, three mineralogic types are identified by a typomorphic mineral, which determines the pigmentation of epigenetically unoxidized rocks: 1) kaolinite — white (members I-II); 2) hydromicaceous — green (member III); and 3) sulfidic — gray (member IV).

The main component controlling the primary reducing properties of a lithologic environment — organic matter — is distributed as coaly detritus unevenly in the bed. Ordered accumulations in the form of thin coal interlayers are observed only in the two bottom members. Here, C_{org} content in rocks with disseminated coaly remains is 0.05–0.07%; in the sands of member IV it drops to 0.03% and less.

Varieties with boulders and "shreds" of clay rocks exhibit sharply higher reductive properties among sandy sediments regardless of mineralogic type; usually, they contain up to 0.1% C_{org} in coaly matter.

Iron content in the rocks is highly variable (from 0.4 to 1.8%). Maximum concentrations are observed in sandy rock varieties enriched in roundstones and "shreds" of clay. In the balance of the iron form, the pyrite component usually plays an important role: it accounts for 10 to 50%, with the proportion increasing up the section from 18% in the bottom member to 40% in the top member — opposite to the behavior of Fe_{gross} : from 1.2 to 0.8%.

Pyrite segregates in the Cretaceous-Paleogene consist of several morphologic varieties. Combined with the relations of this mineral with other rock components, it can be viewed as a genetic indicator (Fig. 2).

The first type (see Fig. 2a) is coarse and fine crystalline pyrite closely associated with organic matter. It forms phytomorphoses after coaly remains and abundant insets in the rocks near the latter. It also grows over clastic grains of heavy fraction minerals. This variety is of a micronodular texture: the central portions consist of framboidal pyrite, while the outer layers are concentrically zonal. The micronodules typically grow together to form larger aggregates.

This pyrite is found in unoxidized sediments of the three lower members, but not in the fourth member. Apparently, it is the earliest variety formed during diagenesis of sediments.

The second type is fine- and small-grained crystalline pyrite, exhibiting no direct correlation either with coaly matter or with areas of epigenetically altered rock. The morphology is similar to the previous variety, except for combinations to larger aggregates. Like the pyrite of the first type, it is found in unoxidized sediments of the three lower rhythms.

The third type is pyrite with fine or cryptocrystalline structure (see Fig. 2b). It is often found in association with pyrite of the former two types, but mostly as independent sooty segregates coloring the rock gray or dark gray. Its distribution is not modulated lithologically. Furthermore, the largest accumulations of this pyrite are observed in sandstones of most permeable sediments of member IV, which are virtually free of coaly matter. It occurs there often in association with brown iron hydroxides. The area of pyrite accumulations of the third type tends toward the central part of the deposit, the one most disrupted by tectonics.

Isolates of pyrite of this type appear as spots, "arches," cutting across the strata and exhibiting concentrically zonal structure. Pyrite forms equigranular aggregates; no zonality is observed in individual crystals, even after double etching. This form seems to indicate a fast precipitation of the mineral from solution.

Besides filling intergranular space, pyrite forms abundant insets in clastic biotite flakes. The large number of inclusions, which often overfill clastic flakes, blur the original contour of these flakes; they swell and, from compact dark-gray units, are converted to a fine-flaked greenish-gray or gray mass.

The fourth pyrite type consists of small- and fine-grained crystalline equigranular aggregate with zonal inner structure of crystals (see Fig. 2c). In contrast to the first two types, there are no micronodules with framboidal central portions. The position of this type of pyrite in the section is strictly determined: it contours ore-forming zones of formational-groundwater oxidation.

The fifth type of pyrite consists of unusual forms: slightly flattened hexagonal prisms linked pairwise by facets (0001) (see Fig. 2d-f). Thin platelets are squeezed between the prisms, usually protruding beyond prism edges. The peculiar crystalline form of pyrite may be due to pseudomorphoses of iron monosulfide, including pyrrhotite after pyrite segregates. Its distribution in the rocks shows a spatial correlation with pyrite of the third type.

The position of iron sulfides in the section of sand-clay fully devoid of organic matter rules out the development of pyrites of the fifth type by biogenic sulfate reduction during sedimentary diagenesis. It suggests a genetic relationship to sulfur brought in from the basement through faults. An epigenetic origin of this sulfur is indicated by the absence of a correlation in the specimens between iron contents (both gross and pyrite iron) and organic carbon (Fig. 3a), in contrast to observations in other metalliferous objects [7]. This is supported by the absence of a relationship between the reductive capacity of rocks [3] and content of organic matter (see Fig. 3b), as well as the existence of a hardly discernible correlation iron contents and reductive capacity in sediments of the lower members and a clear manifestation of such a relationship in member IV (see Fig. 3c); in the latter, no coaly matter or related diagenetic pyrite has been found.

The distribution of iron-containing minerals in ore-bearing sediments and the relationship between pyrite and iron hydroxides were used as a basis for defining types of epigenetically altered rocks. The classification took account of rock color, quantitative characteristics of organic carbon and iron contents, the degree of alteration of the main rock-forming components, and the correlation of the types with uranium accumulations. A level-by-level mapping of lithologic-geochemical types indicated a sequence of postsedimentary rock alteration and pinpointed the place of ore-forming processes in that sequence. In a generalized form, four stages of epigenetic alteration were distinguished, including two oxidative and two reductive stages (see Fig. 1).

The first stage of postdiagenetic alteration was that of formation of a regional zone of ground oxidation (see Fig. 1, I), which corresponds in time to the beginning of the orogenic development of the territory. After the tectonic calm that set in after the completion of the formation of the Cretaceous—Paleogene sediments, the mountain structures surrounding the depression rose during the Middle Eocene. This activated the movement of groundwater, forming a ground flow controlled by levels. As a result, a platform zone of yellow limonitization was formed at the top of the section, nearly parallel to the ancient post-Middle Oligocene leveling surface. The stage was prolonged and comprised the Oligocene epoch: from the beginning of accumulation of coarse-grained sediments of the suborogenic formation until they were covered by the Lower Miocene lake clays.

In terms of geological structures, the deposit area at the beginning of suborogenic formational accumulation was a bowl with slightly concave layers of ore-enclosing deposits. The lower boundary of the in-ground oxidation zone crossed at a small angle the levels of isolated stratigraphic subdivisions. Reconstructions indicate that the boundary on the flanks of the deposit occurred at depths of 75–80 m beneath the roof of the sand bed in low-permeability rocks of the second member; in the central lowest-subsided portions it passed at a depth of 10–20 m in loose sediments of the fourth member. The reduced thickness of oxidized rocks in this direction is not lithologically justified. Besides the

elevation-controlled nature of the oxidation zone under the interruption, it corresponds to areas of synsedimentary tectonic faults which ducted rising reducing solutions; the solutions contained the development of in-ground-infiltrational oxidative epigenesis (with formation of sulfides of the second and third types).

The in-ground-oxidation processes endowed the permeable rocks with brownish mustard-yellow, light-tobacco, and greenish-yellow colors. The epigenetic nature of the latter is indicated by a concentration of iron hydroxides around clay shreds, spotty isolates of iron hydroxides replacing pyrite overgrowing ilmenite grains or hydromica fragments. The pseudomorphous type of limonitization is established on relict structures of iron disulfides preserved in iron hydroxide aggregates.

Besides its powdery and cryptocrystalline forms in interstitial spaces, goethite is found also in clastic micas as well crystallized starlike yellow and lemon-yellow aggregates.

The main ore concentrations of uranium were formed at the lower boundary of the in-ground limonitization zone along gray rocks. The uranium mineralization was of a cloaklike morphology, which has survived; in plan, it is stretched as an oval along the axis of the negative structure. Following the general configuration of the in-ground-oxidized zone, the metallization was distributed in echelons from the lower members on the perimeter of the deposit area to the upper levels in its central parts. Highest uranium concentrations were formed where the limonitization zone was crossed by gray sandstones with clay roundstones and shreds and interlayers of coaly matter with a heightened reductive capacity. When the lower oxidation zone boundary passed through homogeneous alluvial sands it remained virtually devoid of ore.

Uranium mineralization localized in gray rocks near the contact with oxidized rocks was associated with accumulations of selenium and pyrite bordering the limonitization zone as a dark gray up to 1 m thick fringe.

The second stage of epigenetic alteration occurred during the sagging of the territory and formation of the late basin in the Miocene (see Fig. 1, II). Accumulation of thick suborogenic molassoids involved a change in hydrodynamic conditions in the northern part of the depression: instead of infiltrational, it became exfiltrational. This resulted in widespread reductive epigenesis, as hydrogen sulfide fluids rose into oxidized rocks. In-ground oxidized rocks in parts of the deposit were reduced, forming pyrite of type III. The processes were especially intense in tectonically disrupted zones, where waters of deeper circulation were discharged more aggressively. In the foci of intense reduction, rocks became gray or dark gray; on the perimeter they were of a dirty yellow color.

Inverse color relations of rocks with different permeabilities is typical for secondary reduction zones. Roundstones, interlayers, and shreds of oxidized clays on contact with secondarily reduced sandstones have a rim of epigenetic sulfidization. Pyrite often penetrates also inside the roundstones through microcracks. In the coarse-grained relatively permeable part of the section, neomorphous pyrite does not always represent a complete reduction of the rock. For example, cryptocrystalline pyrite grows over sand clastic grains colored yellow by iron hydroxides; sometimes it envelops goethite pseudomorphoses after diagenetic pyrite.

In addition to the conventional methods of identification of "buried" oxidation zones, two additional characteristics were discovered as a result of prolonged and detailed lithologic and mineralogic observations. Pyritized rocks that experienced earlier limonitization were characterized by: 1) a complete absence of framboidal pyrite forms of the first type, and 2) occurrence of crystalline goethite inclusions in clastic micas.

Secondary pyritization was manifest in member IV in the central, most subsided, part of the deposit over an area of 6 km², where long-lived faults are traceable. Currently, this source of reductive epigenesis is of a relict type; originally, the influence of reducers was apparently much broader, as evidenced by swellings of unoxidized rocks in portions of flexural-rupture zones.

The activity of rising reducing solutions caused a burial of some of the in-ground infiltrational mineralization, probably with some redistribution. In the central part of the deposit at the base of member IV, minor (a few hundredths of a percentage point) uranium concentrations separated from limonitized rocks can be traced in the lower side of the reconstructed in-ground oxidation zone.

The third stage of epigenetic alterations is associated with tectonic activation of the region during the Middle and Late Pliocene, which created favorable conditions for infiltrational oxidative processes. As a result, epigenetic limonitization spread and acquired a bed morphology. Widespread interformational erosion resulted in the absence of consistent aquiclude layers in the section; it was responsible for oxidative processes inherited from the ancient in-ground oxidation but with development of indistinct "tongues" of limonitization on isolated highly permeable layers (see Fig. 1, III).

The development of a younger zone of formational limonitization is underlined by several features indicating a redistribution of ancient uranium concentrations and creation of new ore bodies. By several methods (geochemical, mineralogic, radiometric, and paleodosimetric), we determined that the development of formational limonitization increased the thickness of preoxidized rocks in peripheral parts of the deposit by some 20 m (Fig. 4). The boundary of the ancient in-ground oxidation zone is registered by accumulations of brown iron hydroxides marking the former

sulfidization rim of previously limonitized rocks. The level corresponds to a sandstone layer with roundstones and "shreds" of clay, with coaly remains, sometimes not fully oxidized. It can often be traced by residual accumulations of uranium (up to a few hundredths of a percentage point), heightened radium concentrations (radioactive equilibrium factor 1000%), radiogenic lead (up to $1-2 \times 10^{-4}\%$ as opposed to $2 \times 10^{-6}\%$ in the metallization zone), and higher radiation defects of quartz grains (up to 110 relative units, as compared with 30-40 relative units in younger mineralization zones). On most of the deposit formationally oxidized rocks are similar in mineralogy and geochemistry to their older in-ground oxidized analogues. One can identify only young limonitization zones developed after gray rocks; they are distinguished by a greenish-yellow light color with spotty distribution of iron hydroxides.

This formational oxidation stage is clearly seen on areas of previous reduction sulfidic epigenesis. Complex structures of iron hydroxide isolates (across stratification) inheriting the archlike distribution of cryptocrystalline pyrite are indicative of this phase. In such areas the lower boundary of the formationally oxidized zone is shifted to a higher stratigraphic level. The zone itself acquires a tongue-shaped form and is inscribed in plan into the occurrence contour of in-ground oxidized rocks (see Fig. 4), wedging out into the secondarily reduced rocks of the top of the fourth member.

The development of the formational oxidation zone after pyritized rocks is associated with the creation of new uranium mineralization body inside the fourth member. The metallization occurs only on the eastern flank of the reduction source, directed opposite to the flow, that moved southwest and west. The association of uranium metallization with the secondary reduction barrier is emphasized by finds of roundstones and clay shreds with limonite relicts and crystalline goethite inclusions in clastic micas.

The fourth stage of epigenetic processes corresponds to the Quaternary, when Neogene sediments were covered by low-permeable Quaternary proluvial formations with a carbonate cement; it is associated with resumption of activity of rising reducing solutions — in this case of slightly hydrogen sulfide or "grey" type. They formed yellow-gray, pale gray, white, and greenish-earthy pigmentation of rocks and hexagonal pyrites. The alterations were more widespread in plan than pyritization of the third stage.

At the center of the deposit, the reductive alteration zone in member IV cuts across the zone of earlier formational oxidation. The secondary pyritization region penetrates oxidized rocks throughout the thickness here (see Fig. 1, IV). Outside this area, on lower stratigraphic levels, reductive epigenesis gray increased rock thickness by at most 5 m in the vertical section. As a result, brown iron hydroxides marking former diagenetic pyrite accumulations in rocks with abundant clay roundstones and coal interlayers disappear or are replaced by brown-earthy varieties. The pigmentation represents impregnation of rocks with humic acids isolated from coaly matter accumulations.

In whitened portions of secondarily reduced rocks, clay roundstone or shred surfaces and ilmenite clastic grains are free of iron hydroxides. The latter remain only in biotite grains and coaly residues.

The interrelations of the formations of later reductive epigenesis and preceding metallization stage are expressed differently in different parts of the deposit. At the center, where rising reductive solutions had a higher sulfide content, ore bodies formed at the wedging-out areas of formational oxidation in member IV were buried. In the peripheral parts these rising solutions were apparently less reductive and, besides "burying" uranium ores, they partially destroyed them. In many instances, no metallization is observed here on the contact of the oxidation zone and rocks favoring ore deposition: sands with a large number of clay roundstones and coals. Humic acids in such cases were released from the coal, apparently helping lixiviation of uranium and its migration in the reductive setting as uranyl humates.

The activity of rising hydrogen sulfide solutions intensified the reductive properties of terrigenous sediments, retained gray rock areas against the background of the in-ground oxidation zone, and reduced previously oxidized lithologic varieties, forming zones of superimposed pyritization. As a result, two controlling factors appeared in the distribution of mineralization in this deposit: lithologic-geochemical and geological-structural.

The lithologic-geochemical factor determines the position of the metallization in the lower members. It controls its formation at the conjugation of limonitization zone boundaries with rocks rich in coaly matter and higher primary reducing properties. The longer the contact between oxidized and coal-bearing rocks, the wider the metallization placer. There is a direct correlation in the ore between organic carbon and uranium contents (see Fig. 3d), observed also in other infiltrational deposits [7]. The ore bodies are of a lens or bed type.

The geologic-structural factor determines the localization of deposits in secondary-reductive rocks of the upper member. The morphology of the ore bodies is of a roll type; most uranium is confined to the bags in the roll. There is no correlation between organic carbon and uranium in these ores; the higher uranium concentrations are localized in rocks with low C_{org} (0.03-0.5%); on the other hand, there is a direct correlation between uranium content and sulfide sulfur in the ore specimens (see Fig. 3d, e).

The fact that relatively rich uranium metallization is controlled by epigenetic pyrite accumulations raises the question of the possible role of this mineral as a reducer of uranium in exogenous settings.

The question is still being debated. Evseeva and Perel'man [2], Granger and Warren [13], and Rafal'skii [8] support this hypothesis. On the other hand, experiments by Vasil'eva [9] showed that "geochemical pyrite" rocks when sterilized did not produce a drop of Eh of the medium required for uranium precipitation. According to Lisitsin [1, 6], equilibrium Eh in hermetically sealed pastes with pyrite powder are in the range of +150 to +100 mV, which is insufficient for reductive precipitation of uranium from groundwater.

The authors of [5] drew an opposite conclusion from a decrease in redox potential to -200 mV in a column filled with pyrite powder by percolating through it a solution of uranyl nitrate. They observed a drop of uranium concentration in the solution from 5×10^{-3} to 1×10^{-6} g/liter, accompanied by an isolation of uranium oxides which corroded the pyrite grains.

Without claiming a definitive decision of this question, which requires further experimentation and theoretical analysis, we may say that in the specific conditions of this deposit pyrite accumulations in near-fault sources of reductive epigenesis can well support intensive ore precipitation. Zones of epigenesis pyritization of gray and previously oxidized rocks are an important metallization-controlling factor in this deposit and, therefore, could and should be utilized as an exploration criterion and as an indicator in identifying commercial infiltrational placers of ores in rocks poor in syngenetic uranium reducers or containing no reactive organic matter at all.

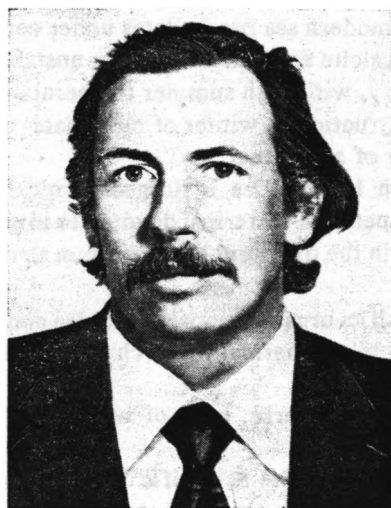
This deposit was formed as an exogenous-epigenetic ore object of a complex classificational type. Metallization was formed here during two main stages of oxidative epigenesis: 1) in-ground-infiltrational (Eocene—Oligocene), and 2) formational-infiltrational (Middle to Late Pliocene), and was polychronic. Two varieties of infiltrational uranium metallization in the rocks are distinguished: a) with syngenetic uranium reducers (coaly matter), and b) with epigenetic reducers (pyritization zones). The first variety is controlled by lithologic—geochemical factors occurring at sites where in-ground and subsequent formational oxidation boundaries cut across unaltered gray rocks with a high reductive potential and rich in organic matter.

The distribution of ores of the secondary variety is motivated by the structural factor and is independent of the primary geochemistry of the surrounding lithologic environment. The reductive geochemical barrier in this case in near-fault zones of epigenetic pyritization formed by two stages of activity of rising hydrogen sulfide solutions.

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VIKTOR IVANOVICH DVOROV



Soviet Geology has suffered a major loss: on September 20, 1987, the young talented scientist—investigator Viktor Ivanovich Dvorov died suddenly. He was a secretary of the Scientific Council in geothermal research of the Soviet Academy of Sciences, and a candidate of Geological and Mineralogical Sciences.

Viktor Ivanovich lived for only 44 years. In his brief career he contributed much to the development of hydrogeochemistry and geothermics. His innovative and comprehensive scientific research included the following topics: the distribution and evolution of thermal metalliferous waters and brines; mobilization, migration, and accumulation of metallic elements in sedimentolithogenesis process; energetics and hydrogeochemistry of the littoral hypergenesis and diagenesis of marine sediments. V. I. Dvorov's pet project was the investigation and extraction of valuable chemical and thermal resource components from thermal waters.

After graduation with a medal from high school, he studied geology at the M. V. Lomonosov State University, Moscow. Dvorov's thesis, devoted to the geochemistry of fluorine in thermal and the other types of natural waters, was awarded the medal: "For the best scientific student work in the USSR." In 1967 Viktor Ivanovich was accepted for postgraduate work in the Institute of Ore Deposit Geology, Petrography, Mineralogy, and Geochemistry of the Soviet Academy of Sciences. The subject of his candidate's dissertation, defended under the guidance of corresponding member of the Soviet Academy of Sciences F. K. Shipulin was: "Geochemical characteristics of the formation of thermal metalliferous brines of Cheleken." This work was published as a monograph in 1975 and brought him wide recognition. For the first time V. I. Dvorov gave an analysis of the geochemical evolution of metalliferous thermal brines in Cheleken, examined the main characteristics of distribution of the range of chemical elements in brines, and in red terrigenous sedimentary rocks, and proved a possibility of the exogenous removal of ore-forming elements (lead, zinc, copper) from the holding rocks.

In 1974 V. I. Dvorov began working at the Geological Institute of the Soviet Academy of Sciences, and in 1976 he became an associate professor and scientific secretary of the Scientific Council of the Soviet Academy of Sciences in geothermal research. He successfully combined his scientific and organizational activities. The range of Dvorov's scientific research was extremely wide.

One of his subjects was investigation of the present hydrogeochemical process in Mesozoic and Cenozoic precipitates of the East Carpathians. V. I. Dvorov was primarily interested in the geological activity of underground gas-water solutions and its role in the process of formation and destruction of hydrogen and some other minerals. He first investigated in detail the sulfuric supergene metamorphism in conglacareous tufaceous rocks of the Transcarpathians, which contain concentrated or dispersed sulfides. Analyzing the stability of the mineral associations,

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he thermodynamically calculated the physicochemical balance of the oxide, carbonate, and sulfide-sulfate natural mineral-forming systems. His hypotheses, expressed in the monograph "Hydrogeochemistry of the East Carpathians," as well as other publications, still have scientific and practical value.

V. I. Dvorov's gas-hydrogeochemical investigation of the modern process in the deposition of the inland (Caspian and Black) seas occupied a main place in his scientific activity. On the basis of experimental, theoretical and field studying of the system: rock-gas liquor, Dvorov for the first time developed thermogeochemical models. He determined the formation of two predominant energetic levels, potentials of which were controlled by iron and sulfur systems and the formation of manganous carbonate in a modern sea precipitates under conditions of a normal sedimentary mass and low temperature. He also proved that iron calcite and sulfite form an unstable mineral phase in littoral sediments with low winter temperatures and, on the contrary, with high summer temperatures they become stable. The correlation of the process of formation in summer and destruction in winter of carbonates and sulfides is such, that the accumulation is taking place gradually in the active layer of sediments.

In his 1st years V. I. Dvorov began to organize hydrogeochemical research on the scientific-research ship "Academician Nikolai Strakhov." He participated in two trips, devoted to investigation of the physicochemical situation of modern sedimentogenesis and diagenesis in the different ocean bottom structures. Some of these results have already been published and others will be soon.

V. I. Dvorov was very active in scientific-organizational work. He conducted many conferences of the Scientific Council of the Soviet Academy of Sciences in geothermal research all over the country, and coordinated the work of different organizations dealing in this field.

V. I. Dvorov authored over 40 scientific works, most of which won awards. His untimely death interrupted his doctoral dissertation project.

Viktor Ivanovich was an active member of the Scientific Popular Society "Znanie" (Knowledge). One of his scientific popular books, written jointly with I. M. Dvorov: "Thermal Waters and Their Use" (1976) won an award from the Society.

V. I. Dvorov was not only a talented scientist, he was involved with art, music, and poetry. He was the center of attention, very popular with his friends and co-workers.

Everybody who lived and worked with Viktor Ivanovich Dvorov — from the field worker to the prominent scientist — remember him as a very kind, enthusiastic, and hard working person. Like this he will remain forever in the hearts of his friends, associates, and students.



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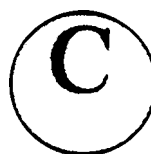
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